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CONTENTS

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Industrial Uses for Cane Sugar:

Removal of Thiophene from Benzene by Catalytic Hydrogenation:

American Contemporaries:

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THE LISTENING POST

Overheard about This Issue

Aluminum Sulfate manufactured at the water treating plant and fed into the water directly in the form of solution saves money in the operation of the Dalecarlia filter plant supplying water to Washington, D. C., according to Lauter (page 953). A detailed analysis of the cost of the operation is given to show how economically this simple chemical conversion of bauxite to aluminum sulfate solution can be accomplished in a water treating plant.

Handling Hydrocyanic Acid, whose reputation as a poison has placed it almost in a class by itself, has always appealed to chemical engineers as close to the absolute zero of jobs. Yet, in describing its manufacture in considerable detail as carried out in a plant producing tons of it, Carlisle (page 959) makes the statement, surprising to most of us, that in the plant described "not a single man has lost his life or had his health permanently impaired." That is a record of which one may well be proud, and particularly is it a cause for congratulation of those responsible for the design of the plant itself. Even the most enthusiastic Californian has yet to claim that the perfect climate of his state is a cure for hydrocyanic acid poisoning!

* * *

Cane Sugar, despite its too well-established reputation as a mere sweetening agent, appears in a new role as a potential raw material for chemical synthesis. Cox, Dodds, and Ferguson (page 968) describe syntheses in which sugar's property of sweetness has given way to its alcohol groups by allowing it to form esters with fatty acids and in which levulinic acid, formed directly from sugar, is the parent of a series of interesting and perhaps valuable alkyl esters. Again we are reminded that things are not always what we have believed them to be, especially when research begins to reveal their true nature.

Synthetic Resins possess properties which from their very nature are subject to close control as our knowledge of them grows. Kienle and Schlingman (page 971) in continuing their discussion of alkyd resins make an opportunity to review the general theory of resin formation and to apply this to the property of flexibility.

In Nitric Acid Manufacture from sodium nitrate, the precise point of cut in the distillation is of prime importance in securing a high yield of first grade product. To make the determination of this point exact and easy, Coster (page 980) uses an electric conductivity cell which follows exactly to concentration of the distillate. Not only does this technic avoid delay in sampling and testing, but it has wide application in other fields in simplifying control procedure.

Detective Story Readers will find in Waters' paper (page 1034) on the disappearance of blue dye in old writing, much food for thought. Perhaps a Conan Doyle or a Wilkie Collins among our readers may develop a good murder plot on the basis given here.

Strawberries, we learn from Fellers and Mack (page 1051), not only contain vitamin C but retain it even when frozen to strawberry ice cream, a comforting thought for a hot day.

Complete Utilization of the heat of a flame by burning fuel actually within the body of a liquid to be evaporated is only one of the advantages of submerged combustion described by Kobe, Conrad, and Jackson (page 984). Applied to viscous liquids and those tending to form scale deposits when evaporated in the ordinary way, the new technic avoids a vast amount of trouble for the operator. Even so troublesome a mess as sulfite pulp waste liquor readily succumbs to the efficiency of submerged burners and evaporates with a heat efficiency of better than 90 per cent, a figure to be reached in ordinary practice only in some undiscovered Utopia of engineering where every condition is ideal.

Rubber Technology has been advancing by giant strides under the impetus of the automobile's demand for better and better tires, and, as improvements have followed one another in controlling the fundamental reaction of vulcanization, new methods have been quickly adapted to plant practice. Jones (page 1009) continues his series on the mechanism of the reactions involved in vulcanization with a discussion of the action of multiple accelerators, now so important in the industry.

In Much the same field, Allen and Schoenfeld (page 994) go into the question of the role of gas black in a rubber compound.

What Happens to Gas forced under pressure into an old oil well? The answer to this question vitally affects the use of gas under pressure to put new life into debilitated oil pools and involves the possibilities of getting more oil from known areas. Pomeroy and his co-workers (page 1014) give us part of the answer from their study of solubility rates of methane in hydrocarbons.

Purification of Benzene, especially freeing it from thiophene, is of primary importance in its use in chemical manufacture. Pease, Keighton, and Munro (page 1012) have applied the modern methods of catalytic hydrogenation to this problem with interesting results.

* * *

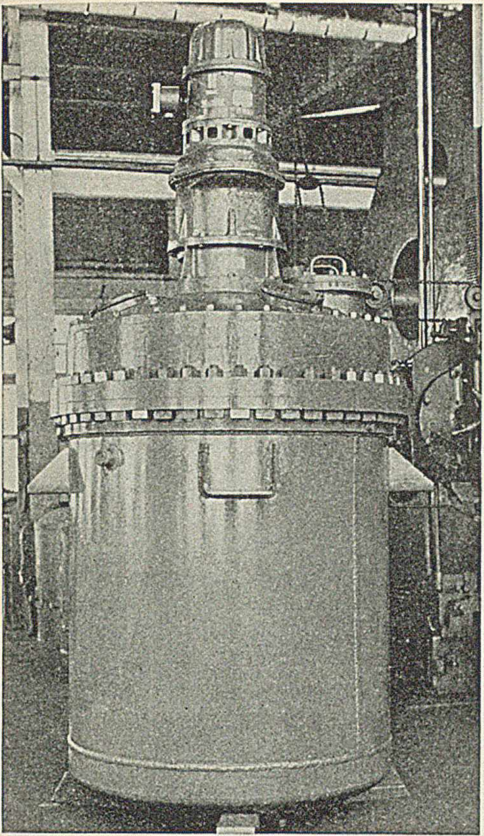
Utilization of Waste Sulfite Liquor, containing a large part of the material of the original wood treated, has been one of the vexing problems of the paper industry. Phillips (page 991) has subjected the solid residue from evaporating this waste to destructive distillation and reports his findings here.

New Resins Made from Glycerol, described by Ushakov and Obriadina (page 997), supply a means of modifying the properties of the well-known phenol-aldehyde resins for special purposes. These Russian investigators give us not only methods of making the new resins but also a considerable amount of information as to their applications.

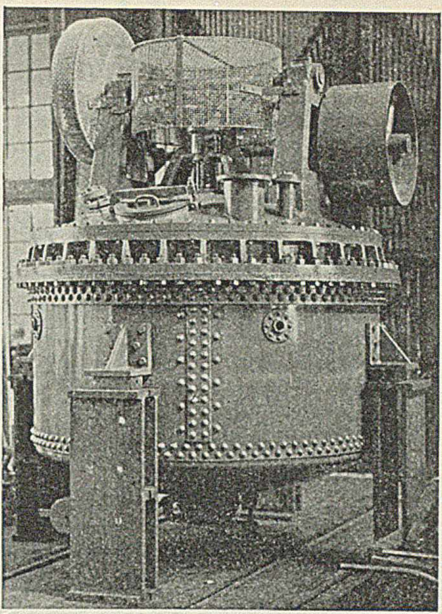
Lime Treatment of municipal water supplies to reduce corrosion of pipe systems is discussed by Hopkins (page 1050), who gives figures from the experience of the city of Baltimore to substantiate its value.

Guidance for Universities in seeking research problems of industrial importance is provided by Rose (page 1028), who includes a number of suitable subjects related to dyestuffs which come within this category.

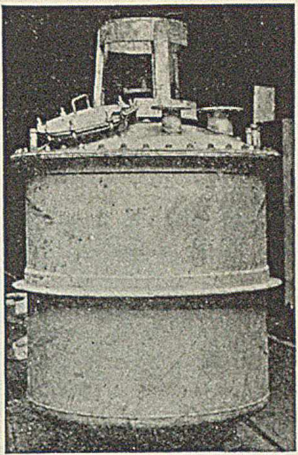
FIGHTS
CORROSION
at
LOWER
COST



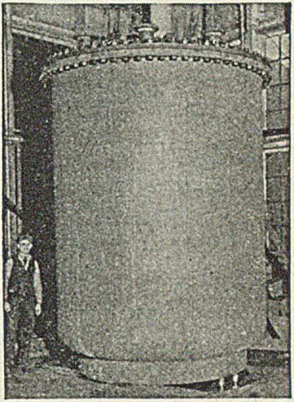
A jacketed kettle designed for 175 lb. steam pressure equipped with a horseshoe type agitator operated by a vertical geared motor drive.



A high pressure jacketed mixing kettle with 1,200 gallon capacity used for processing a phenolic compound.



A stainless steel reaction kettle equipped with 3 blade stainless steel agitators electrically driven through a speed reducer.



A rubber lined cast iron kettle with cover designed for 90 lb. working pressure.

BUFLOVAK

PROCESSING KETTLES

BREWERY EQUIPMENT

*DRYERS

*EVAPORATORS

*IMPREGNATORS

*FUMIGATORS

*VULCANIZERS

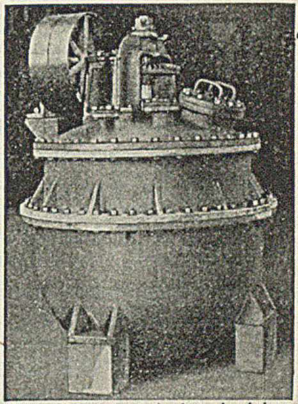
*CHEMICAL PLANT EQUIPMENT

CHEMICAL CASTINGS

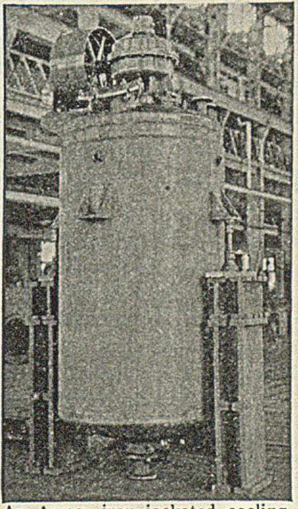
* Fabricated wherever practicable from any of the new materials of construction.

THESE illustrations show a few of the many type BUFLOVAK and BUFLOKAST Processing Kettles. They serve a wide group of industries for still a wider number of processes. Quite naturally they are built in a large number of sizes and designs including cast iron, sheet steel, stainless steel, copper, aluminum, nickel clad and lead lined. They can be furnished for vacuum, atmospheric or pressure operation and employ various heating mediums such as direct fire, steam, hot oil and mercury vapor.

Where particular requirements cannot be fulfilled with standard equipment the large variety of drawings and patterns which we have on hand often permit a modification with a substantial saving in construction costs. Copy of bulletin 227 will be sent upon request.



A cast iron steam jacketed mixing kettle with power driven agitator built in 11 standard sizes for either vacuum or atmospheric operation.



An Armco iron jacketed cooling kettle with gate type agitator, 4 ft. diameter x 7 ft. deep.

BUFFALO FOUNDRY & MACHINE CO.

1549 Fillmore Ave., BUFFALO, N. Y.

NEW YORK
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ST. LOUIS
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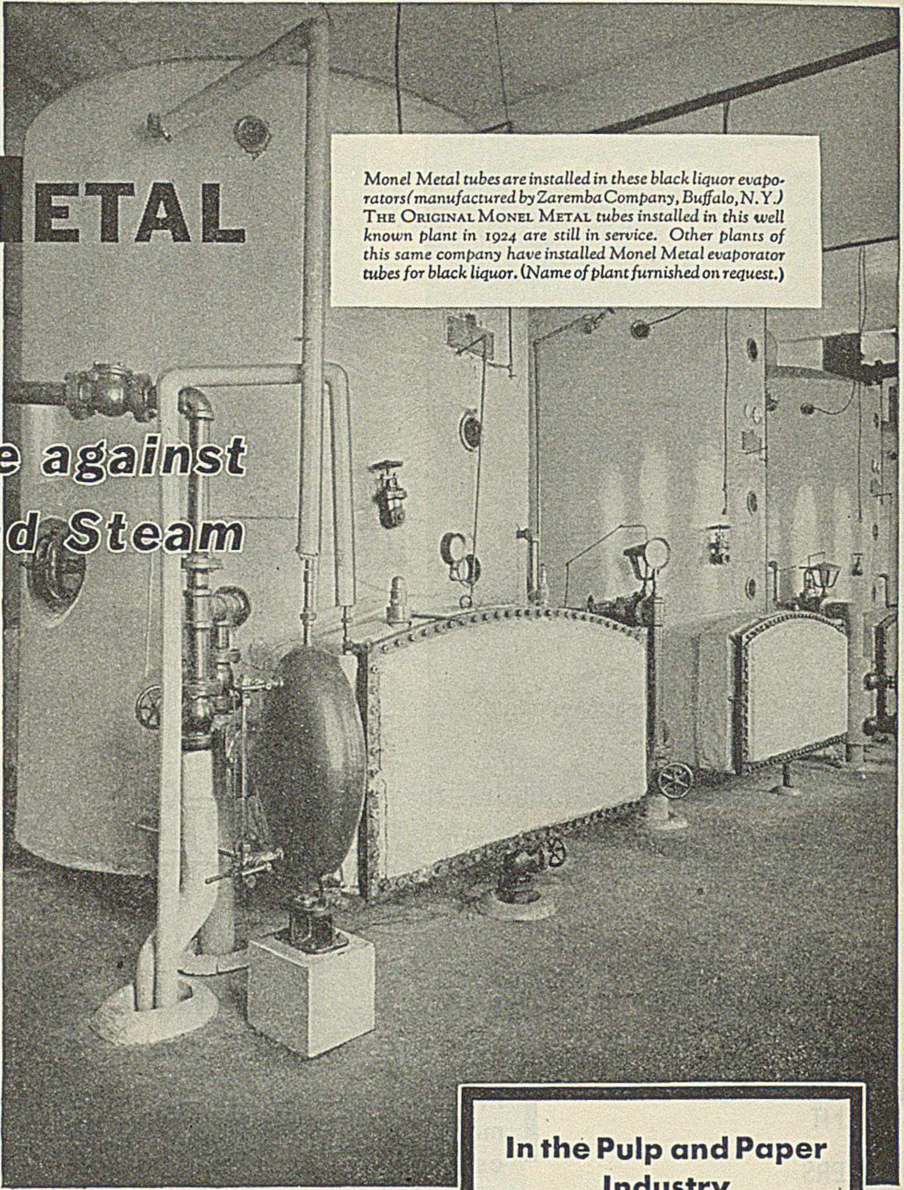
MONEL METAL TUBES

win 9 Year Battle against Black Liquor and Steam



Monel Metal tubes are installed in these black liquor evaporators (manufactured by Zaremba Company, Buffalo, N. Y.) THE ORIGINAL MONEL METAL tubes installed in this well known plant in 1924 are still in service. Other plants of this same company have installed Monel Metal evaporator tubes for black liquor. (Name of plant furnished on request.)

WELDED MONEL METAL TUBING FOR BLACK LIQUOR EVAPORATORS

In the pulp and paper industry, the cost of frequent replacement of black liquor evaporator tubes is an important item. The high cost of metal tubes resistant to both the black liquor and steam has up to now discouraged their wide use. Monel Metal tubes last for years in this service.

Recent developments in the manufacture of lower-priced welded Monel Metal tubing have opened the way for the wide use of Monel Metal welded tubing for black liquor evaporators. Monel Metal welded tubing with thoroughly sound, strong and ductile welds is now available in various wall thicknesses and in a wide range of sizes.

The excellent resistance of Monel Metal to caustic solutions, in combination with splendid mechanical and physical properties, make Monel Metal welded tubes ideally suited for black liquor service. Longer life, fewer replacements, reduced maintenance costs and improved efficiency are a few of the advantages. Monel Metal welded tubes have been used in black liquor evaporators since 1924 and have proven far superior to the charcoal iron tubes commonly used.

Complete information regarding sizes available, together with prices, gladly forwarded on request.

MONEL METAL FILTER CLOTH

In paper mills filter and wire cloth must withstand both corrosion and abrasion. This problem is further complicated by the necessity of protecting the product against discoloration.

Because Monel Metal combines in one metal the strength of steel with great corrosion-resistance and long life, it is employed by the most modern paper mills in the country.

Monel Metal woven wire cloth and winding wire are helping paper mills to produce a more uniform and better product at lower cost. They are helping to reduce waste...to recover a higher percentage of clay and fibre. Monel Metal woven wire cloth is used for:

- Cylinder moulds
- Lime mud filters
- Bleach washers
- Black liquor filters
- Brown stock washers
- Wood pulp washers
- High density thickeners
- Cylinder paper machines
- Save-alls
- Deckers
- Salt filters
- Screens

Send for new booklet, "What Metallic Screen and Filter Cloth Offer Your Plant."

MONEL METAL PUMP RODS

The many places in a paper plant where pumps are used make it necessary to reduce pump rod and shaft costs as much as possible. Monel Metal rods help you to do this. With Monel Metal you can be sure there'll be no rusting, scoring or pitting of the rod. You can be sure, also, that the glass-smooth surface of Monel Metal will reduce friction and wear, thereby cutting packing costs. The long life of Monel Metal pump rods and their low maintenance costs more than justify their use.

LITERATURE on Monel Metal Pump Rods available on request.

In the Pulp and Paper Industry

MONEL METAL IS WIDELY USED FOR:

Evaporator Tubes
Cylinder Mould Rods (5/16″)
Wire and Filter Cloth
Winding Wire
Screens
Jordan Engine Fillings
Couch Roll Stay Rods
Suction Box Stay Rods
Save-all Trays
Suction Box Trays
Table Rolls
Pump Rods and Shafts
Valves and Fittings
Alum and Size Tanks

• • •

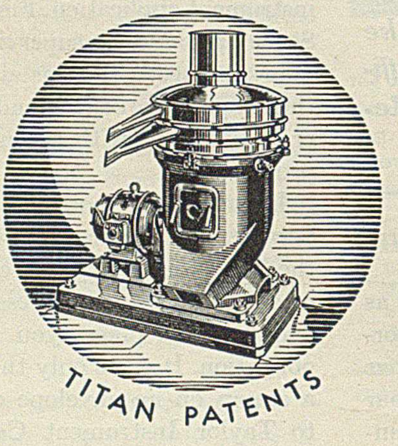
Monel Metal is a registered trade-mark applied to an alloy containing approximately two-thirds Nickel and one-third copper. Monel Metal is mined, smelted, refined, rolled and marketed solely by International Nickel.

MONEL METAL

THE INTERNATIONAL NICKEL COMPANY, INC.

67 WALL STREET, NEW YORK, N. Y.

260
250
240
230
220
210
200
190
180
170
160


TITAN PATENTS

Baker's P-6

[BUTYL ACETYL RICINOLEATE] . . . a new castor oil derivative with great possibilities

▲ Three years of successful use in the industrial field have made it advisable to offer our Baker "P" line of castor oil derivatives to the trade.

Listed here are 17 of these new Baker alkyl ricinoleates which have a wide range of commercial applications. In addition to their well-known ability to impart flexibility and stretch to pyroxylin compositions, these modern castor oil derivatives have many other uses. They may be used as extremely high boiling and low freezing solvents, general plasticizers, dispersing and grinding media, etc.

Other suggested applications include their use as emulsifiers, detergents and "wetting out" agents. As top-cylinder lubricants and agents for lowering the co-efficient of friction of mineral oils, these materials should be of great interest to the lubricating field. *However, since each derivative possesses distinctive properties, the particular problem will determine the proper choice.*

Our research department will be glad to cooperate with you in recommending suitable applications. Just write or phone us at the address below.

BAKER'S "P" LINE
of Alkyl Ricinoleates

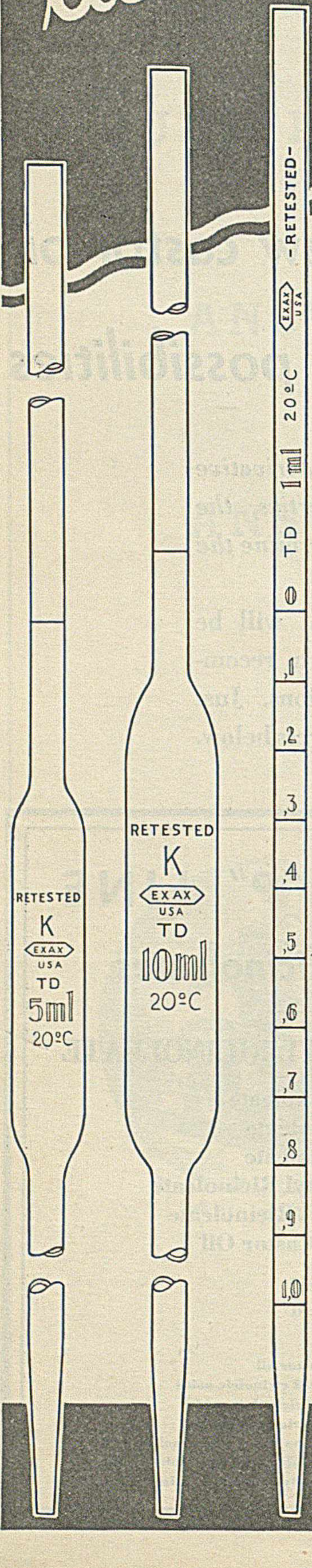
P-6–BUTYL ACETYL RICINOLEATE

P-1–Methyl Ricinoleate
P-2–Ethyl Ricinoleate
P-3–Butyl Ricinoleate
P-4–Methyl Acetyl Ricinoleate
P-5–Ethyl Acetyl Ricinoleate
P-8–Acetylated Castor Oil

P-10–Ricinoleic Acid
P-20–Ricinoleic Acid

P- 7–methyl undecylineate
P- 9–acetylated polymerized castor oil
P-11–methyl ester of polymerized ricinoleic acids
P-12–ethyl ester of polymerized ricinoleic acids
P-13–butyl ester of polymerized ricinoleic acids
P-14–methyl ester of acetylated polymerized ricinoleic acids
P-15–ethyl esters of acetylated polymerized ricinoleic acids
P-16–butyl ester of acetylated polymerized ricinoleic acids

THE BAKER
CASTOR OIL COMPANY
120 BROADWAY, NEW YORK, N. Y.
Plants . . . . Jersey City and Bayonne, N. J.
Research Laboratories . . . . Jersey City, N. J.



RETESTED
K
EXAX
USA
TD
5ml
20°C
RETESTED
K
EXAX
USA
TD
10ml
20°C
-RETESTED-
EXAX
USA
20°C
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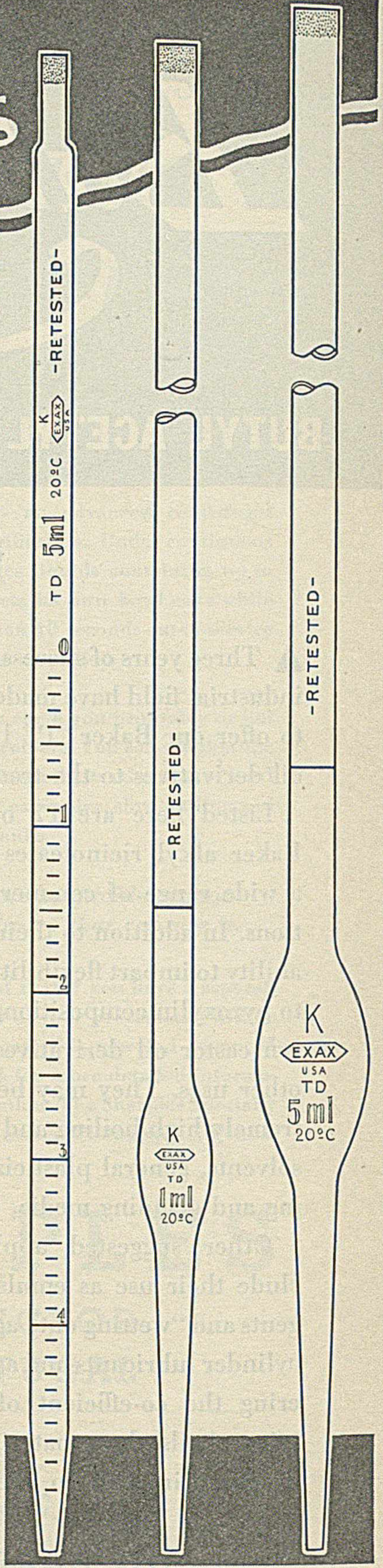

-RETESTED-
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USA
20°C
5ml
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1
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3
4
-RETESTED-
K
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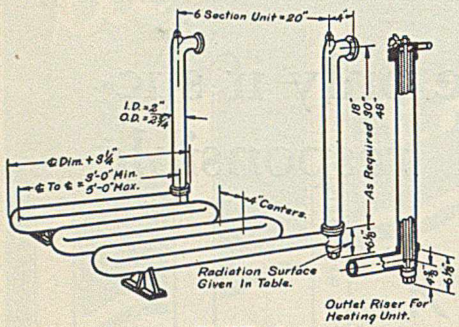
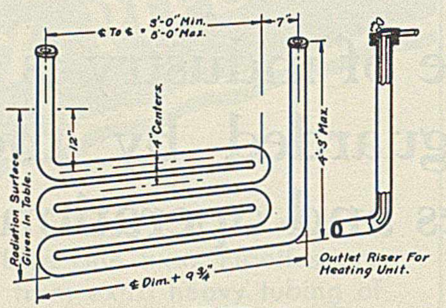
USA
TD
1ml
20°C
-RETESTED-
K
EXAX
USA
TD
5ml
20°C

Does your process require this kind of equipment?

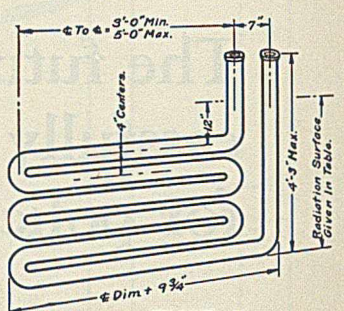
DURIRON HEATING OR COOLING COILS



TYPE-1

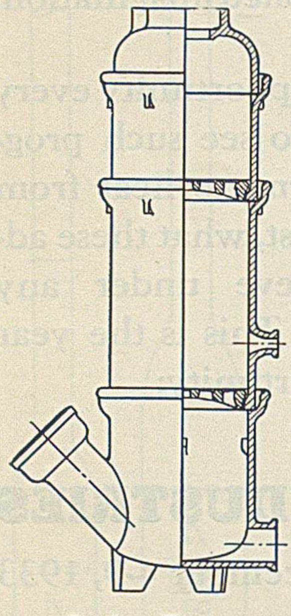


TYPE-2



TYPE-3

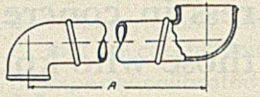
Cast sections are readily welded into various forms of heating or cooling units, submerged joints being eliminated and the welds are as acid-proof as the casting. Standard sections can be welded into a variety of forms to suit particular requirements



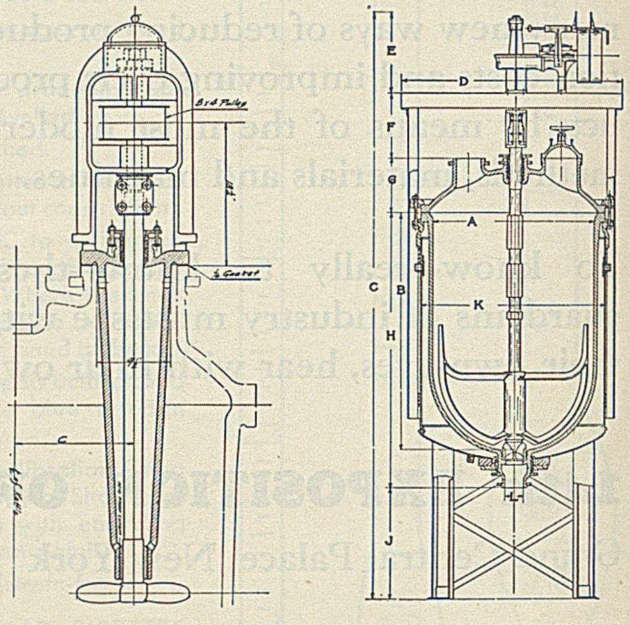
Duriron Tower

Duriron Bleaching and Denitrating Towers are available in sizes from six inches to three feet, inclusive, in diameter, with all necessary grids, fittings and connections.

Duriron S-Bend Condenser Tubes



I. D.	"A"	Effective Cooling Area Outside (Sq. Ft.)
1½″	39″	2.1
4″	60″	7.1
6″	60″	10.4
6″	72″	12.3
6″	84″	14.2



Duriron Stirrers and Agitators, with either Duriron or Durimet shaft, are available in scraper and high speed offset propeller types, either belt or motor driven. Duriron Kettles are available in from 1 to 650 gallons capacity, plain or jacketed. Write for Bulletin 157 for complete data.

DURIRON is resistant to practically all commercial corrosive chemicals. Because of this, it has proved in many processes to be the most economical to use.

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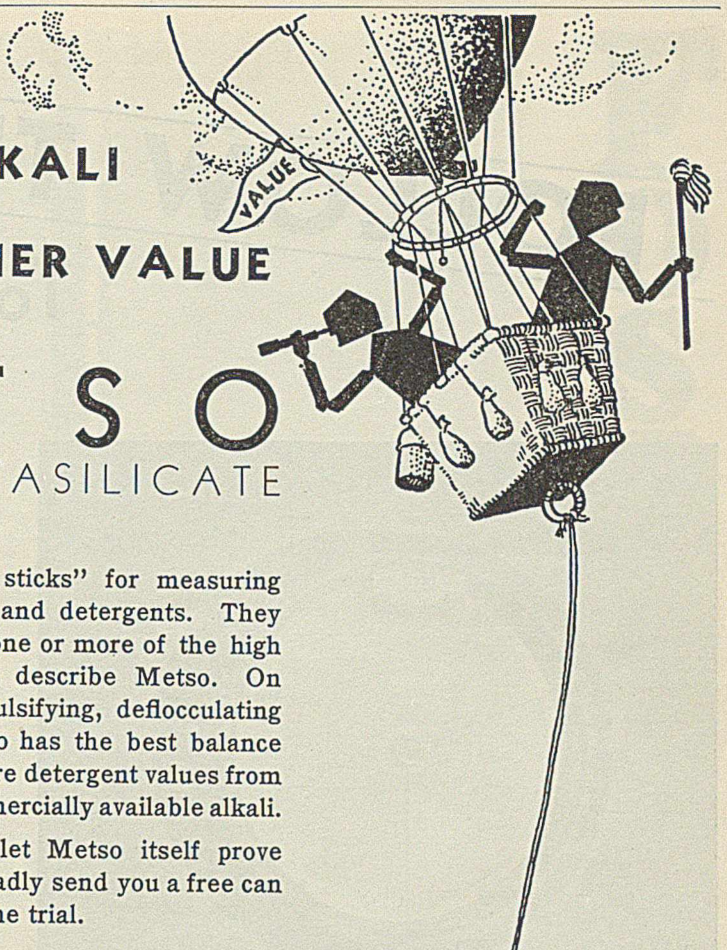
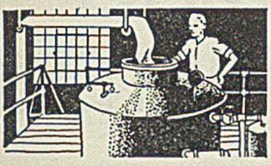
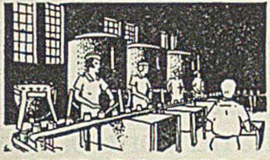


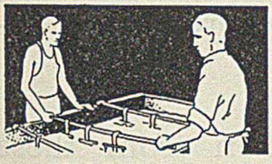
THE NEW ALKALI THAT PROVED ITS HIGHER VALUE

METSO

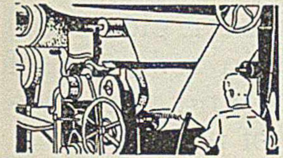
SODIUM METASILICATE


TEXTILE MILLS


FOOD PACKERS


METAL PLANTS


LAUNDRIES


PAPER MILLS

YOU have your "yard sticks" for measuring the worth of cleaners and detergents. They undoubtedly include one or more of the high points listed below which describe Metso. On every count—wetting, emulsifying, deflocculating and dissolving power Metso has the best balance of properties. You get more detergent values from Metso than from any commercially available alkali.

Check the list, and then let Metso itself prove these claims. We shall gladly send you a free can of this new detergent for the trial.

1. High wetting power. In wetting glass, for instance, Metso has higher power than other alkalis.
2. Good deflocculent. Field experience proves Metso to have superior merit in preventing redeposition of dirt.
3. Metso emulsifies fat, oil, grease, forming stable oil-in-water emulsions.
4. Metso yields solutions of higher pH than other alkalis except NaOH, which strength is sustained until alkalinity is almost completely neutralized.
5. Metso provides inhibiting effect, which makes it adaptable for cleaning soft metals, fabrics, glass.
6. Metso is a free rinser.

Metso is pure sodium metasilicate, $Na_2SiO_3.5H_2O$, originated and developed by us after extended research (U.S. Pat. 1898707). It is available in over 65 cities. Prompt deliveries everywhere.

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☐ May I have information on Metso for..............................

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

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City..............................

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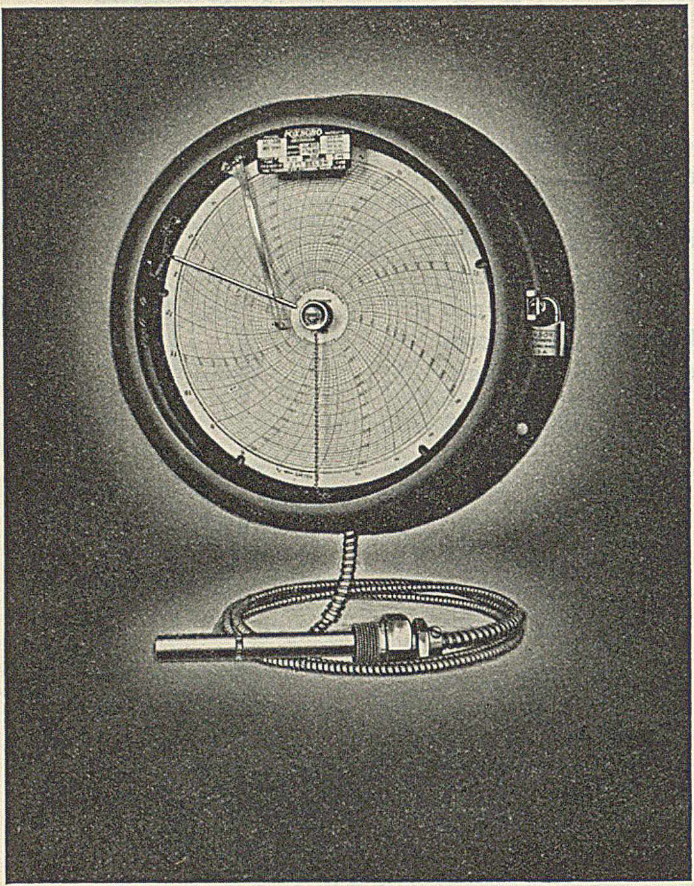
To Better Hand Control with FOXBORO RECORDING THERMOMETERS



The Foxboro Recording Thermometer

Some Typical Uses For Recording Thermometers in Chemical Plants

EVAPORATORS
DRYERS
STILLS
ACID COLUMNS
COATING PANS
DEHYDRATORS
CALCINATORS
CONCENTRATORS
TANKS
KETTLES

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REG. U. S. PAT. OFF.
THE COMPASS OF INDUSTRY

◈ Improved regulation of process temperatures results in more economical production and more uniform product. Automatic control is often desirable but hand control can be improved easily and economically with Foxboro Recording Thermometers.

◈ The records taken from these instruments show the TREND of the temperature changes and thus enable the operator to correct variations quickly and accurately.

◈ Foxboro Recording Thermometers make hand control easier, closer and surer. This results in reduction of waste and spoilage, and improvement in the quality of product.

◈ The premium now placed on quality as the result of the "new deal" makes it important that you should know more about "improved hand regulation." WRITE FOR FOLDER NO. 615—NO OBLIGATION OF COURSE.

THE FOXBORO COMPANY, FOXBORO, MASS.
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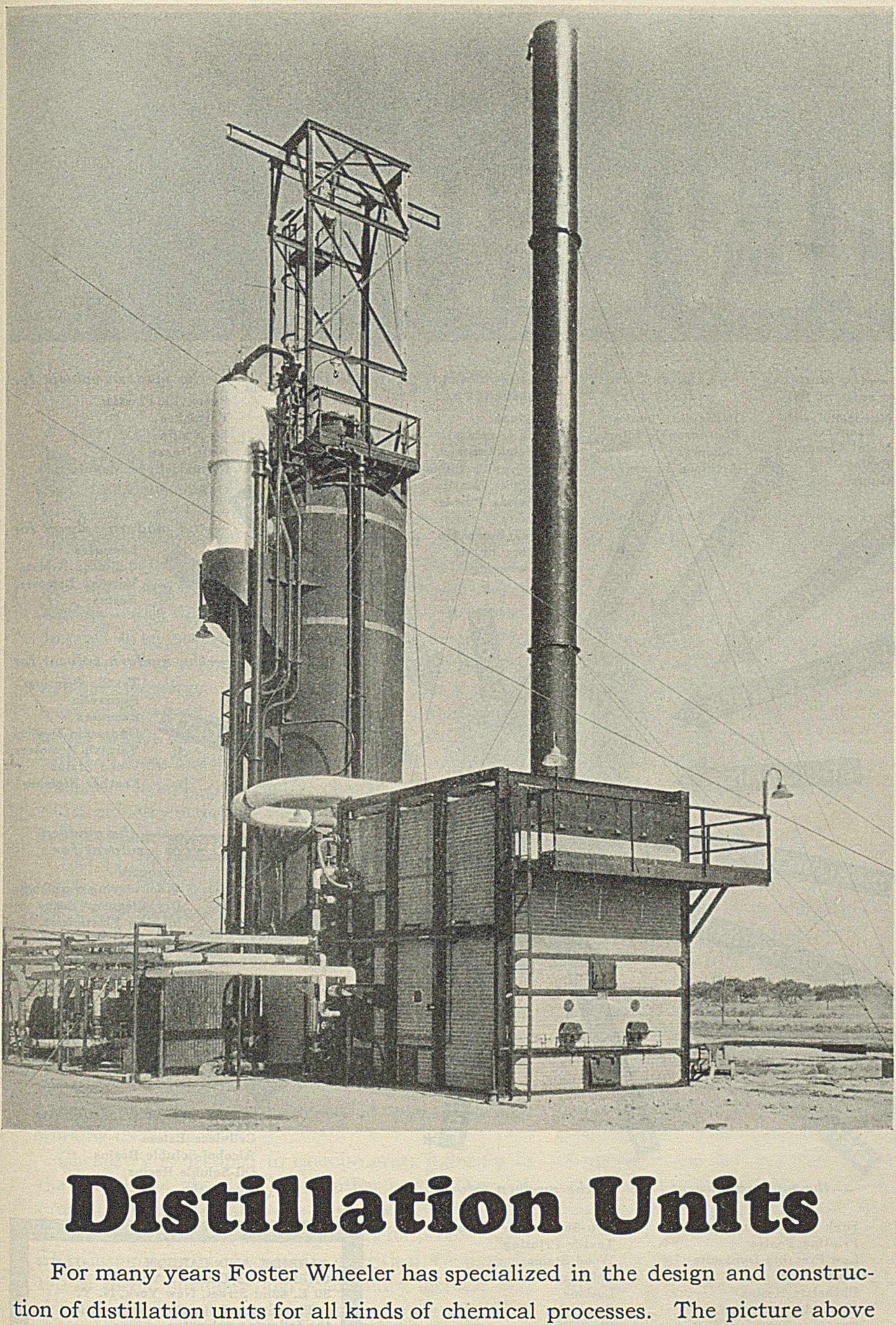
. . . *Complete Industrial Instrumentation* . . .



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Casein
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Cosmetics
Rust Inhibiting

—the modern solvent for
Nitrocellulose Lacquers
Metal Cleaners
Resins
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—the modern solvent for
Pyroxylin Plastics
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—the modern solvent for
Acetylene
Rayon (Acetate)
Artificial Leather
Photographic Films
Pyroxylin Plastics
Smokeless Powder
Lacquers
Varnish Removers
Spotting Fluids
Oil Dewaxing

—the modern solvent for
Gums
Alkaloids
Essential Oils
Cosmetics
Dehydration
Antiseptics

—the modern solvent for
Pyroxylin Plastics
Varnishes
Dyestuffs
Anti-freeze
Formaldehyde Manufacture

—the modern solvent for
Degreasing
Oil Dewaxing
Alkaloid Extraction
Acid Concentration

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HARRISON E. HOWE, EDITOR

The Editor's Point of View

SCIENCE IN STABILIZATION. Efforts to stabilize industry, to increase employment, and to augment payrolls are guided to some extent by landmarks established in the past, but the success of the plan depends in large measure, not on the old, but on the new. Industries, like individuals, grow old, and with increasing age there is a fixity of ideas and change becomes more difficult to undertake. After a time industries even seek political interference against the competition of younger enterprises and strive to maintain the *status quo*. Control, with which goes a certain measure of security, is always more welcome to an industry which has become static than to one bristling with new ideas and still plastic enough, not only to welcome, but to seek, constructive change. The extent to which industry maintains research and utilizes its results is one measure of its youth.

Just a little consideration will show how impossible it is to proceed far with our sights trained on the past. If there were no other factors, the research laboratories of the world, and especially those devoted to chemistry, are sufficient to force us to right-about-face. During the past four years science has continued its march, creating new opportunities, contributing many improvements, and unavoidably making necessary the abandonment of some processes and equipment. Recovery acts cannot be interpreted as protecting obsolescence, and science may be depended upon to continue working its changes.

Chemistry is destined to exercise great influence in the period just ahead, if for no other reason than because it is fundamental to the processes by which what the world offers is changed into what its people want. The consuming public becomes more critical of commodities as their abundance and availability increase and the improvements demanded generally require chemical research. Accelerated consumption may threaten the existence of an important material, and research is engaged much more frequently in creating equivalents than in finding substitutes.

The scientist hesitates to assume the role of a prophet, but his faith in things that can happen is strengthened by what has taken place within a decade—yes, even within a year. Such events appear of minor importance to the average man, yet their aggregate motivates industry and supports that acceleration in the supply of goods and services which gives stability to prosperity. From whatever angle one may view the future, science will be as important, indeed more important, as it has been in the period with which we are so familiar. No scientist holds that we have achieved the ultimate, though he himself may be unable to see from what direction the next move is to come. There is every reason to believe that the influence of research, which cannot be subject to code, will be of increasing importance as our requirements change and as our civilization attains higher levels.

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CHEMISTS UNDER THE NRA. While the several groups of manufacturers who comprise the chemical industry, specialty manufacturers, and builders of chemical equipment, are perfecting organizations and preparing to submit codes for approval, the individual chemist in many instances is left wondering how he is affected. Title I of the National Industrial Recovery Act is concerned almost wholly with "trade or industrial associations or groups" and does not touch upon professional activity. Furthermore, the President's blanket code, quite generally signed in advance of special codes for a particular industrial trade or group, does not take into account professional employees. Where industries have prepared a code to be substituted for the President's blanket code provision may have been made for professional workers, and it is contemplated that the permanent codes, of which there are very few thus far, will take such employees into account. In Article I of the code submitted by the Chemical Alliance, "employees" is defined to include all persons and in Article II anyone employed in an executive, administrative, supervisory, and/or technical capacity, or as an outside salesman is exempt from the limitations as to hours.

In these circumstances the individual chemists who are interested should look to the codes affecting the industries where they are employed to ascertain their status under them.

Several firms of consultants and analysts employing staffs of workers of various grades, the majority of which are now paid well above anything contemplated in the codes, have signed the blanket code referring to hours of work and to payrolls, so that they are doing their part. Where the consultant is practicing individually in his own name, it is clear that the President's Reemployment Agreement does not apply. In Section 4 it is stated that "The maximum hours fixed in the foregoing paragraphs shall not apply to employees (in certain places) nor to registered pharmacists or other professional persons employed in their professions." It is hoped that a better situation may eventuate with respect to fair and proper charges for analytical and testing work, the basis for which quite obviously is a sound and uniform method of costing. If the code could accomplish this result it would be received with acclaim. An involved part of the problem is that touching those activities of staff members of educational institutions, which compete in analysis, testing, and even development and consulting work.

It is generally recognized that the NRA program, which has made wonderful strides and has already accomplished certain miracles, cannot as yet be called wholly successful. To make it succeed in the full sense of the word is the earnest objective of millions of our people. No alternative is offered. The plan must be carried to success. All are urged to do their utmost to achieve it.

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A MODERN CANUTE. Among technical men trends in fixed nitrogen have become so well known that further discussion seems out of place. The public, however, continues to be interested and is likely to be misled. The press carries accounts of efforts to reorganize the Chilean nitrate industry and of repeated attempts by the European synthetic industry and the Chilean nitrate industry to reach some accord intended to control the world nitrogen market and avoid a price war. The object seems to be to command the waves of progress and the result will doubtless compare favorably with that achieved by Canute of old.

It is small wonder that Chile is wellnigh desperate. Prior to 1914 she produced more than 60 per cent of the nitrogen consumed in the world. This had dropped to 36.4 per cent by 1924, fell to 9.6 per cent in the fertilizer year 1931–32, and will be still lower during the current year. Meanwhile prices have dropped precipitously, and we find the banks which have loaned money on stocks of nitrate becoming more and more nervous. The annual producing capacity for fixed nitrogen in the world exclusive of Chile is estimated at 3,400,000 metric tons of pure nitrogen, while the maximum world consumption including Chilean nitrate was 1,950,000 tons of pure nitrogen in the 1929–30 year. In the face of this Chile had on hand at the end of 1932 stocks estimated at 2,000,000 tons of nitrate in Chile, 1,000,000 tons in Europe, principally in England, and 350,000 tons in the United States. Much of this nitrate was mortgaged to banks against loans and while Chile has never resorted to dumping nitrates, it is conceivable that financial difficulties and the action of the banks may lead to such a course. The attitude of mind is further reflected in an article in *El Mercurio* published in Santiago July 4, 1933, which, in discussing the new corporation that has been formed to take the place of Cosach which sank under the weight of a debt it could not meet, says that "it will fix prices which if possible will bring in a profit, but it will fix prices which above all will permit the sale of nitrate."

Courageous steps have been taken by the Chileans to regenerate their nitrate industry, which is so vital to their country and to their government. But it is futile to hurl challenges at the synthetic industry. Improvements in technic, reduced costs with large volume production, and the capacity for world over-production would be certain to bring further disaster to Chilean nitrate, should an unfortunate price war be undertaken. It may be unpleasant to sense the rising tide, but there is no likelihood that the waves can be controlled.

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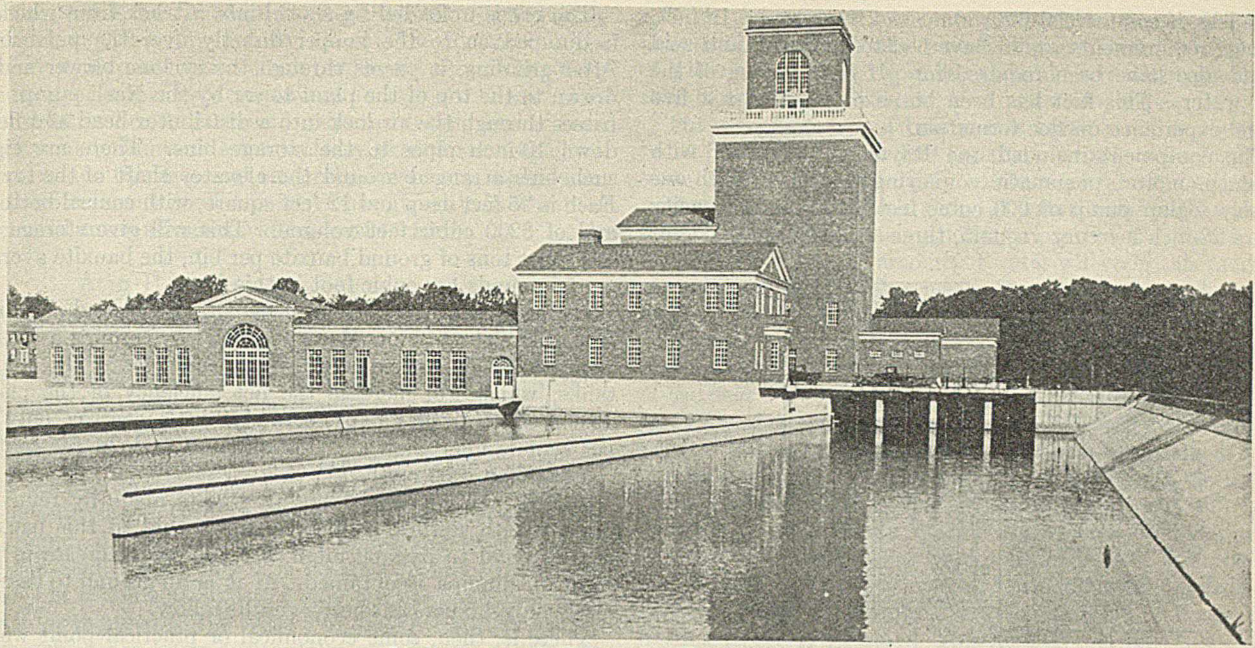
CREDIT THE CERAMISTS. At the Washington meeting of the AMERICAN CHEMICAL SOCIETY a Symposium on Glass was presented, this being a joint effort sponsored by the Glass Division of the American Ceramic Society and the Division of Industrial and Engineering Chemistry of the AMERICAN CHEMICAL SOCIETY, as was widely publicized at the time. Through an inexplicable and unfortunate error, in publishing the papers of the symposium it was not stated that the Glass Division of the American Ceramic Society had collaborated. This is particularly unfortunate since the success of the symposium was due in largest part to the efforts of the members of the Glass Division, many of whom are also members of the AMERICAN CHEMICAL SOCIETY. The way for the symposium was made clear by the coöperative action of Emerson Poste, then president of the American Ceramic Society, and Alexander Silverman, chairman of the Glass Division. F. C. Flint, a prominent member of both societies, did all that any chairman could do to assure a worthwhile program, which was carried through only after those participating in it had conferred in person and agreed upon the scope of each paper.

It is our hope that there may be further occasions for joint symposia held by the two societies which have so much scientifically in common.



Sedimentation Basins at Dalecarlia Plant

Manufacture of Aluminum Sulfate at the Dalecarlia Filter Plant, Washington, D. C.

Carl J. Lauter, Dalecarlia Filter Plant, Washington, D. C.

The manufacture of liquid or sirup aluminum sulfate (17 per cent alumima) is described as made at the Dalecarlia rapid-sand filter plant, which is fed directly as a dilute solution to the raw water for coagulating purposes.

Special points on specifications of bauxite and acid are discussed, and the cost of manufacture based on the results and experiences of the past five years is given.

When the Dalecarlia rapid-sand filter plant was designed in 1925 for increasing the water supply of Washington, D. C., it was decided to incorporate in the structure an aluminum sulfate manufacturing plant based on the process patented by C. P. Hoover. There were about ten aluminum sulfate cake alum plants erected at this time, but little actual data on comparative cost were available although trends seemed to indicate that the proposition to make liquid aluminum sulfate would be more profitable than that using commercial alum or making cake.

The process, in short, is to feed quantities of bauxite into sulfuric acid diluted to 45° Bé. in lead-lined steel tanks, allowing the exothermic reaction to proceed to completion with little or no external aid, then adding water to dilute the sirup to a definite concentration and feeding the same to the raw water according to needs as regulated by laboratory control.

Dalecarlia Plant

The Dalecarlia rapid-sand filter plant, completed and put into service in 1927, has a capacity of 80 million gallons per day, handling Potomac River water ranging in turbidity from 6 to 2000 parts per million of suspended matter as received at the point of application of the coagulant, after preliminary straight sedimentation in the Dalecarlia Lake. The water for the McMillan slow-sand plant, also of 80 million gallons capacity, is likewise given a preliminary treatment at this point with aluminum sulfate when the turbidities leaving Dalecarlia Lake are 100 p. p. m. or more. The combined treatment for these two plants on 80 to 120 million gallons per day total gives a range from 4000 pounds minimum to 33,000 maximum of aluminum sulfate per day.

The rise in turbidity of the Potomac River is also very rapid, often changing from 50 to 1000 p. p. m. in several hours; this requires a great range in feeding facilities of the plant. With only the six boiling tanks of 10,000 gallons capacity each, it precludes the possibility of using a more dilute solution than 7 per cent aluminum sulfate at all times.

Definition of Alum Sirup

Alum or aluminum sulfate in this article means a sulfate containing 17 per cent water-soluble or available alumina. This is not the theoretical aluminum sulfate with 18 molecules of water of crystallization and molecular weight of 667, but one which has a resulting molecular weight of 600. By using this formula the product can be more equitably compared to commercial filter alum, which is generally specified for, and contains 17 per cent of available alumina.

All calculations are made on this basis, and this makes prices 10 per cent higher than if computed on the basis of theoretical aluminum sulfate with 18 molecules of water; yields are proportionately lower.

Plant Equipment

The cost of the original equipment for the manufacture of aluminum sulfate only, installed in 1927 when prices were at high levels, amounted to $56,000 in round figures. This was exclusive of any buildings which would have been very little less, if commercial filter alum had been used. In fact, storage requirements would have had to be larger, and acid would also have been required for pH conditioning of the raw water. This fact has been borne out in the past five years' experience on floc formation.

The equipment included one Raymond pulverizer with 125-h. p. motor, pneumatic conveying machinery with one Nash vacuum pump of 600 cubic feet per minute capacity and a 22-inch mercury vacuum, three steel storage tanks for 60° Bé. sulfuric acid of 150 tons capacity each, three lead-lined steel boiling tanks of 10,000 gallons capacity each, two bauxite weighing hoppers of 4 tons capacity each, two large dial scales attached to the hoppers, two lead-lined centrifugal acid pumps with 5-h. p. motors, acid fume scrubber and sirocco fan, steel acid-measuring tank, piping for air and water, and screw conveyor from hoppers to boiling tanks.

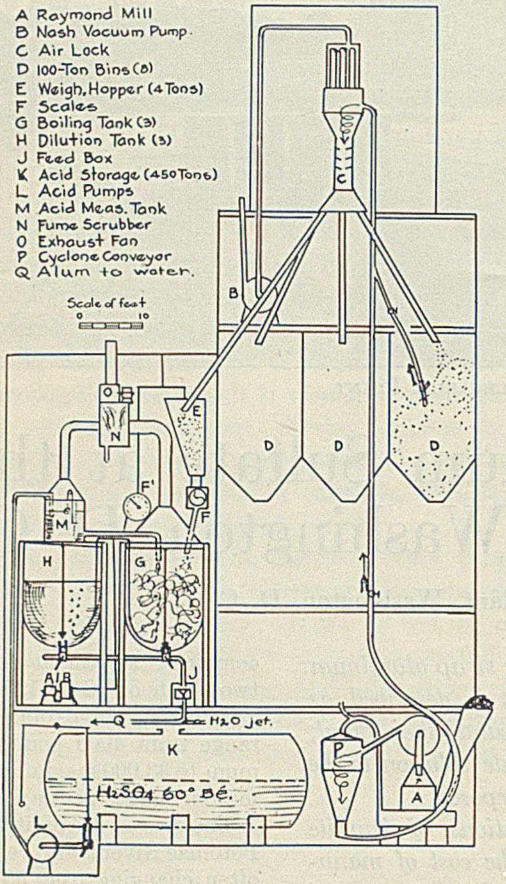


Figure 1. Alum Manufacturing Plant

Since this original installation of 1927 about $12,000 worth of capital investments were added—namely, an additional Nash vacuum pump of 650 cubic feet per minute capacity and with a 26-inch mercury vacuum, operated by a 75-h.p. motor. This is also used for lime transportation although it has been figured in 100 per cent on alum. Two spare boiling tanks were lead-lined and one old one relined, the screw conveyor was extended for the new boiling tanks, and a double pipe line was installed to the railroad siding for acid and lime handling from cars.

These added investments practically double the original capacity which was around 2000 tons of sulfate annually.

Bauxite Handling

All bauxite is received in carload lots and is delivered at the railroad siding located about 1500 feet from the plant proper.

The ore is unloaded by shovel into a truck from which it is dumped on to the hopper directly over the pulverizer. After grinding, it passes through the cyclone blower and is drawn to the top of the plant tower by the Nash pump. It passes through the air lock into a distributor head and flows down 10-inch pipes to the storage bins. There are eight such bins arranged around the elevator shaft of the tower. Each is 25 feet deep and 12 feet square, with conical bottoms and of 3200 cubic feet volume. This will give storage for 100 short tons of ground bauxite per bin, the bauxite averaging 75 pounds per cubic foot in this form.

At the present time 7 tons of bauxite are ground per hour, but alterations to be made will cut this to perhaps 5 tons in order to obtain a more finely ground material for the boiling tanks, which will increase the net efficiency of the plant. The present ground bauxite runs a little coarse; only 57 per cent is finer than a 100-mesh sieve and 28 per cent is coarser than a 60-mesh.

Careful and repeated laboratory tests made by refluxing bauxite with sulfuric acid have shown that, if this bauxite is all ground to pass 60 mesh, a 4 per cent increase in the yield of alumina is obtained. If it is all ground to pass 80 mesh, only 4.5 per cent better results follow.

There is, then, some economical or practical point where the time of grinding will more than absorb the gain in yield, and from the above results it can be deducted that, if all material is made to pass a 60-mesh sieve, it will have been ground fine enough to meet the purpose of aluminum sulfate manufacture. It is also more difficult to handle the finely ground "fluffier" material in the air-conveying system. Trouble of this nature was encountered at the very outset, owing partially to purchase of lower grade ores.

Bauxite Specifications

The first specifications for bauxite called for 50 per cent alumina ore with 2 per cent moisture and some limiting figures on iron oxide. With this, a material was received which ground with much difficulty and to such a consistency that it did not flow properly down the 10-inch distributor pipes into the bins, even at an angle of more than 60°.

It was necessary to supplement auxiliary air jets in the entire conveying system, and a great amount of time and labor was involved in filling the bins and later transferring the material to the boiling room. This transfer of bauxite to the weighing hoppers was first done by means of air conveyors attached to the bottoms of the storage bins. After about a year of difficulties due to arching and packing of material, this method of transfer was abandoned and the ore was then drawn out of the top of the bins by air nozzles, connected to the Nash system; this has proved satisfactory in every respect.

Next orders for bauxite called for 53 per cent, but this has been gradually increased, all present ones now requiring 57 per cent alumina, with a loss on ignition of not less than 29 per cent and a moisture content of not more than 1.5 per cent; an additional clause specifies that ground material passing a 60-mesh sieve shall have an apparent density of more than 1.

Recently a superior grade of bauxite was encountered meeting all of the other requirements and even running less than 1 per cent in moisture, but, after grinding at the usual rate and fineness, it had an apparent density of only 0.6. This was also practically demonstrated when the weighing hoppers suddenly overflowed when only six-tenths of the usual amount of ground ore was placed in them on the initial filling. The figure for density is determined by tightly packing a 2-liter beaker and obtaining the weight relative to water. It is possible to obtain very close checks by this method, and it has imposed no inconvenience or handicap on bidders. This low-density bauxite could scarcely be handled in the pneumatic system but should offer no handicap in bucket or screw type conveyors.

On a lot of South American bauxite running higher than 60 per cent in alumina even better yields of alum resulted, but prices for this material are prohibitive for inland plants, and there are many good deposits of hard bauxite in Arkansas which will meet all specifications satisfactorily.

ACID HANDLING AND SPECIFICATIONS

Sulfuric acid is contracted for in 500-ton quantities of 60° Bé. and is received in carload lots at the plant siding.

Prior to 1932 cars were unloaded by transferring the acid to a small tank truck and hauling it to the storage tanks. This was costly, netting about 75 cents a ton of acid.

In 1932 a 3-inch iron pipe line was laid to the tracks, was fitted with machined joints and lead gaskets, and carried a one-inch air line alongside. These lines are all carried above the ground, and air from a 25-kw. compressor is used to unload the acid. With this it is possible to unload a 50-ton car in 5 or 6 hours at a cost of only 6 cents per ton of acid. All acid is pumped to the three long steel cylindrical storage tanks, which are lying horizontally on concrete saddles, in the basement adjacent to the boiler room of the plant. They are provided with safety lead plug valves on the inside of the tank just over the drains to the pumps. Three-inch Duriron plug valves are used on these drains leading to the pumps, which deliver the acid to the measuring tanks in the boiling room.

Specifications for acid require that it shall be 60° Bé. or as near to this as temperature will permit for shipping without freezing. It shall be arsenic-free, and have no nitrous gases in solution or any white suspended matter, which is chiefly iron sulfate from dirty cars. It is further specified that a 10-ml. sample of the acid from the car shall require less than 0.75 ml. of 0.1 *N* potassium permanganate to oxidize any ferrous salt or sulfur dioxide which might be present. The acid generally requires but 0.40 ml. of permanganate.

It was necessary to add this last requirement to prevent the objectionable odors of hydrogen sulfide and sulfur dioxide which often filled the basement when acid was being put into the storage tanks or being drawn to the measuring tank. This trouble has now been eliminated and the installation of ventilator fans in the storage tank room has removed the last chance for a repetition of this nuisance.

ALUMINUM SULFATE MANUFACTURE

All aluminum sulfate is made by intermittent process or batches and is not a continuous process as in the large chemical manufacturing plants making this product.

This description is of what is called a 12-ton batch, since it is the yield of sulfate; it is the average batch made. Acid is first pumped from the large storage tanks in the basement by lead-lined centrifugal pumps, through 2.5-inch lines to the measuring tank. This is a steel tank, 6 feet deep and 6 feet in diameter, lined by lead spray. It is located in the boiling room at an elevation above the boiling tanks. From the measuring tank it flows by gravity into a measured volume of water in the lead-lined boiling tank. For this batch 1000 gallons of water is the customary amount into which 16,000 pounds of acid are added.

In the meantime, 8000 pounds of bauxite are taken from the storage bins to the weighing hoppers in the boiling room by the pneumatic conveyors, as previously stated. From the hoppers which are suspended above the boiling tanks the bauxite is transferred to the desired boiler by a screw conveyor operated in turn by a 2-h. p. motor.

With the present grade of bauxite this charge of 8000 pounds of bauxite, 16,000 pounds of acid, and 1000 gallons of water yields 24,000 pounds of aluminum sulfate, giving a ratio of 1:2:3 for the bauxite, acid, and alum, respectively.

The actual process of boiling this batch requires about 2 hours from the time the first bauxite is added, to its completion. The reaction is entirely exothermic and requires intermittent quenching with a spray of water from quick-acting, 3-inch valves on the rising mass, to prevent the tank from overflowing. A small amount of water will stem this sudden rise which generally takes place after about one-third of the bauxite has been added. No more water is used than necessary, and bauxite is added as quickly and regularly as conditions will permit. This is to take advantage of all of the heat of the reaction and to obtain a higher yield, which generally averages 90 per cent of the total available alumina.

After the remainder of the bauxite has been added, the boiling continues vigorously for at least 20 minutes, when the mass subsides. It is then slowly diluted to about 30° Bé., at which point it will not solidify when cool. After standing 12 hours or overnight and being well air-stirred, a sample is analyzed by the White method,[1] using barium hydroxide titrations, and then diluted up to standard volumes for feeding to the raw water. This method of analysis is quite rapid and with proper variations is as accurate as gravimetric determinations for alumina. The following sheet was developed in this laboratory:

ANALYSIS DATA

f. of $Ba(OH)_2$ = ...
A. ( ) ( ) = ( ) (0.0078464) = ... g. H_2SO_4 per ml.
B. ( ) ( ) = ( )
C. = A − B = ( ) (0.0081768) = ... g. Al_2O_3 per ml.
D. = C/0.17 = ... = g. 17% alum per ml.
E. = 62.4 (D) = ... = pounds 17% alum per cu. ft.
F. = E ( ) = pounds alum (uncorrected)
Sludge loss = __________ pounds
Pounds yield corrected = ____tons
BATCH DILUTED TO____cu. ft. equivalent to ____ lb. cu. ft. or____ % alum

....

G. (C) (2.88) = ( ) (2.88) = ... = H_2SO_4 equivalent Al_2O_3
H. If acid (A − G) = (......) g. free acid per ml.
(H) (62.4) (orig. diln.) = lb. free acid C. P. 100%...
I. If basic (G − A) (......) ÷ 2.88 = (......) g. per ml.

....

REMARKS:

It is possible to adjust the alum batches to any degree of acidity or basicity to obtain optimum floc formation by simply varying the amount of the acid in the reaction. A solution is generally used which will eventually contain about 1 per cent free acid. It is necessary to do this as the pH and alkalinity of the raw Potomac water fluctuates from 7.0 to 8.3 for pH and from 25 to 130 for alkalinity. Alum dosages vary from 0.7 to 3.9 grains per gallon with an average of 1.5 grains for the Dalecarlia plant.

The strength of the solutions used vary from 7.5 per cent aluminum sulfate at periods of low turbidity and low dosages to 15 per cent at periods of high mud content and higher treatment. All alum is conducted from the dilution tanks to the water through lead pipes fitted with Duriron plug valves. The flow is regulated by measurement over V-notch weirs located in an auxiliary feed box.

In addition to the weir float gages, an additional feature is incorporated on alum feed control which is believed to be original for filtration plant operation. This is a continuous recording Leeds & Northrup pH machine, utilizing the flow type of quinhydrone cell which gives accurate and direct readings of the pH of the treated water about 15 seconds after the introduction of the alum and before any carbon

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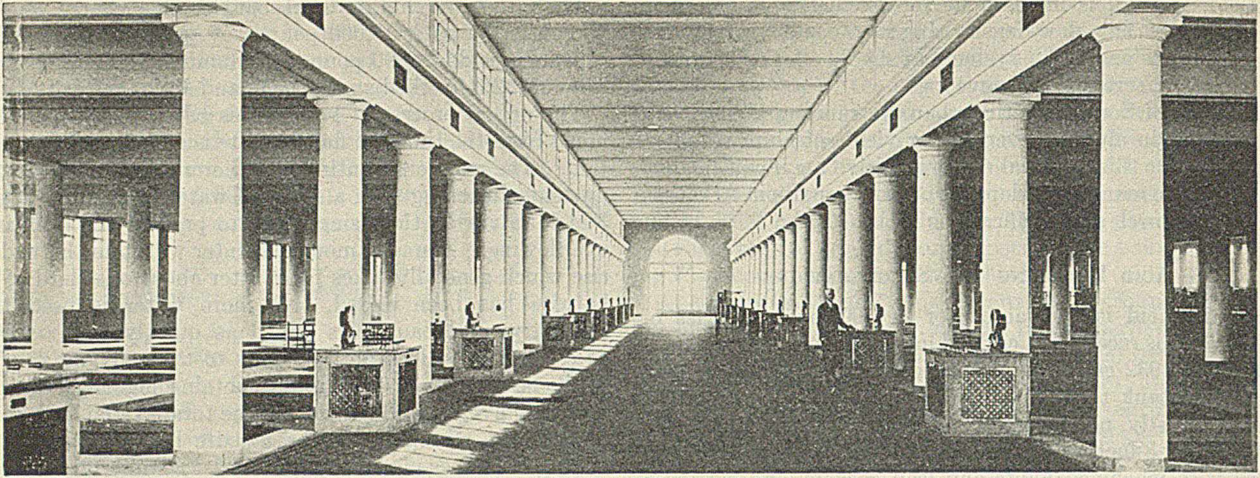
[1] *J. Am. Chem. Soc.*, 24, 457 (1902).



Operating Floor of Filter Room

dioxide can escape from the water. It has proved a delicate check on the treatment and is of special value with this sort of a sirup which contains sludge of varying composition, as is the case with a tank of alum in the course of its flow from a full to an empty tank. As the solution tanks become empty, the concentration of the sludge always increases somewhat, and any device recording only volume of flow would not necessarily record concentration of chemical. The pH measurement does this perfectly, thereby preventing irregularly treated water.

Final filter effluent pH is also controlled by a similar recorder for hydrated lime application, which operates successfully with a quinhydrone cell at pH values as high as 8.4, when this point is necessary. The Leeds & Northrup Company successfully developed this flow type cell at this plant several years ago, using an alcoholic acetone solution of quinhydrone in place of the solid quinhydrone with water passing over or through it. A considerable saving in lime was effected after the installation of this recorder, and similar results are anticipated with the alum control cell, in addition to its primary function of maintaining a uniform treatment at all times.

In the manufacture and application of this aluminum sulfate sirup in which improvements are being made constantly, a considerable sum would have been saved over that required if this plant had been built with the idea of using only commercial filter alum, even if the latter material was contracted for on a long-term order. This is a difficult policy for a government department to pursue.

Some trouble was experienced with lead linings of the boiling tanks, which have all been wiped off the books in three years. The first three tanks put in service in 1927 were lined with eight 10-pound lead sheets; these were hung from the top, being cut in orange peel pattern and carried to the extreme bottom of the tank. The edges of the lead were clamped down with eight vertical steel ribs, 2 inches wide, and these in turn were protected by an 8-inch strip of lead, welded vertically on each edge to the lining.

The bottoms were reënforced with a circular disk of lead, 3 feet in diameter, and a heavy lead casting was placed over the outlet for the seat of the plug valve with which each tank is fitted.

After about one year of boiling the alum mixture, the lead began to sag, and, since lead does not contract to its original form, these sags increased and caused ridges at the bottom of the tank, which had to be cut out and rewelded.

At the point where the lead linings passed over the lapped joints of the steel shell, the constant friction of this expansion actually caused the lead to part in horizontal cracks. This was repaired by welding horizontal bands over these points and extended the life of the lining for another two years, at which time the frequency of repairs necessitated the installation of the two tanks which had not yet been lined.

These two tanks, and later one of the old ones, were lined as is shown in Figure 2. The operation of installing the lead in this manner was somewhat tedious, but, by slotting the bolt holes and uncoiling the prepared lead, it was satisfactorily applied in continuous horizontal bands.

This method gave the minimum of welded joints and at no point did the lead support more than 3.5 feet of weight, the width of the band. In the original tank the strips only had one horizontal support and the stress of 16 feet was imposed on the top edge, although partially compensated for by vertical support.

Two of these new tanks have been in service for two years, and only a few cracks have developed at points where the lead was not hammered back against the tank, just below the rings, thereby allowing a certain amount of hinge action.

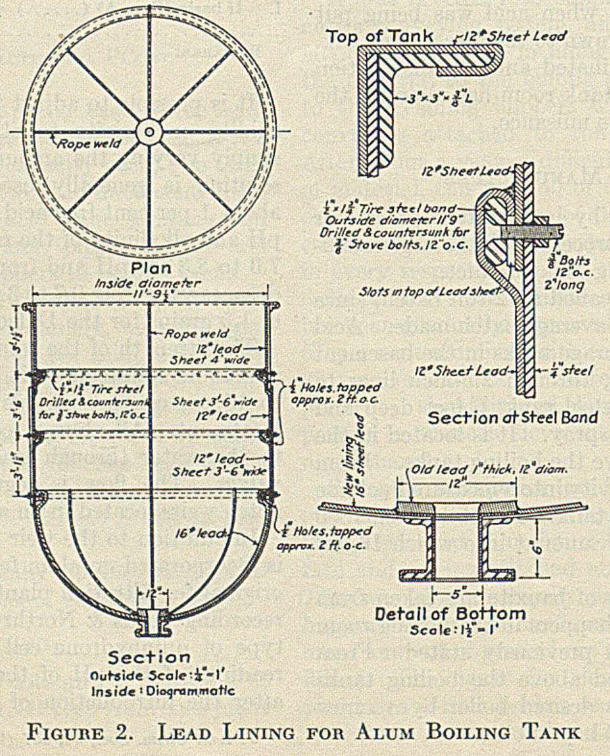
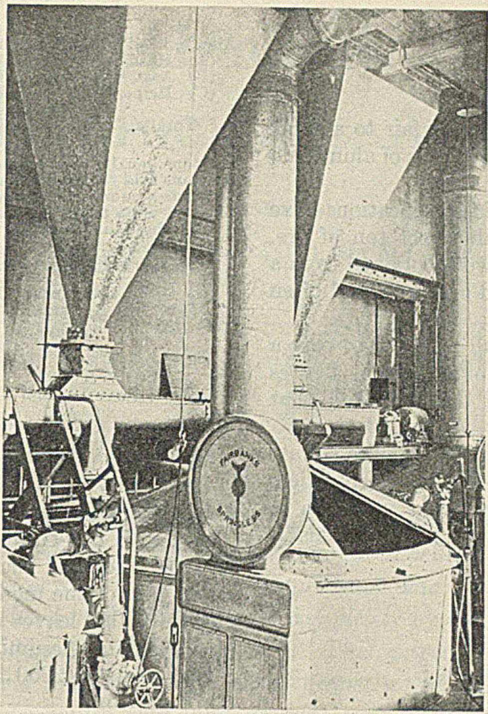


Figure 2. Lead Lining for Alum Boiling Tank

They promise to give the five years of service allotted to them in the depreciation charge.



Alum Boiling Tanks and Bauxite Hoppers

Pipe Line and Handling Difficulties

In the handling of this alum sirup, containing from 5 to 10 per cent of sludge, it is difficult to apply float valves successfully. The sludge will accumulate in any type of feed boxes, and air must be used to agitate the solution.

The first few months of experience with float valves verified this, and feeding was thereafter carried out through a secondary lead-lined box, 4 feet square and 4 feet high. This was provided at first with a slot orifice, but, here again, sludge and one per cent sulfuric acid caused trouble. Finally, a rubber stopper plug fitted to a lead orifice was provided; this proved successful and was used up to January, 1933.

At this date all alum feed lines were replaced with 3-inch solid lead pipe, and a manifold system of such pipe with Duriron plug valves was installed under the six tanks. From this system the alum is now fed through a secondary feed box directly from the tanks containing the diluted sirup. This feed box is simply a small lead chamber, 6 × 12 × 8 inches, with a V notch of 60° at one end.

By floats with suitable gages the flow is easily regulated, and with the pH control on the treated water as an additional check it is possible to obtain an efficiency of almost 100 per cent in the treatment.

In the feeding of this diluted alum sirup to the water, a jet of water is and always has been used with the solution in order to prevent clogging of the lines which are about 200 feet in length and 3 inches in diameter, with only a 1-foot drop in this length. Some of this line was originally of cast iron, but at the elbows this material did not stand up well; this is the part that was replaced with lead. The fiber duct has stood up satisfactorily and is still in continuous service.

Twenty years of life for the alum pulverizer is not too great an estimate, when it is considered that this machine is not used more than 20 days of the year. This machine should give 5 years of service for 200 days, which would provide a life of 50 years for this plant, whereas only 20 years of life are assumed in the depreciation figures. The steel boiling-tank shells are also given 20 years; this does not mean the lead linings, which are only given 5 years, and should even average 7 or 8 years of life.

It was not the purpose of this paper to add any overhead charges, insurance, or taxes. These would be constant for whatever type of coagulant used, and, since these charges vary as to locality, they can readily be calculated on the basis of the figures given for capital investment.

Cost Accounting Statement

The following section, devoted strictly to cost accounting, is self-explanatory. It gives an accurate picture of the experiences of the five years beginning October, 1927, the date of the opening of the Dalecarlia Filter Plant, to July 1, 1932.

There are no cost accounts for buildings or rentals, as equivalent structures would be required for the handling of any other material which could be used as a coagulating medium for water treatment. As a matter of fact, storage requirements for ground filter alum would have to be larger than those provided for bauxite and acid. The plant at present is capable of manufacturing and handling 100 per cent more than is made and used at this time, and with no further expenditures for machinery or buildings.

Interest is centered more in comparative figures, and it is estimated from figures shown below that savings of 10 to 12 thousand dollars a year are obtained, or a net figure of $5.00 for every ton of aluminum sulfate made.

The net cost per ton of aluminum sulfate was $13.00.

The January, 1933, price for 57 per cent grade bauxite was $10.72 per short ton, delivered at the siding. This is $2.38 a ton less than he average on the 5-year operation which included some very high-priced bauxite and acid. The January, 1933, price for 60° Bé. acid was $9.38 a ton, delivered, which is $2.63 a ton less than the 5-year average.

Summary of Itemized Cost Account on Aluminum Sulfate Manufacture

	Cost per Ton of Sulfate Made	
Prime cost bauxite and acid (materials only on basis of 1933 costs and yield)		$10.00
Manufacturing cost:		
Labor:		
Unloading bauxite	$0.170	
Unloading acid	0.027	
Transferring bauxite and acid	0.084	
Boiling process	0.150	
Total		0.431
Power:		
Grinding bauxite	0.100	
Unloading acid	0.013	
Transferring bauxite	0.033	
Stirring diluted alum for feeding	0.180	
Total		0.326
Indirect cost:		
Labor:		
Maintenance of machinery	0.760	
Material replacement	0.210	
Total		0.970
Depreciation on capital investment (on total valuation)		2.210
Interest on capital charges (on total valuation as designated)		1.480
Total cost per ton alum made		$15.417

Note: All costs are on the basis of aluminum sulfate containing 17 per cent alumina.

Prime Cost of Aluminum Sulfate

(Materials only)

Year	Acid	Bauxite	Alum	Acid Cost	Bauxite Cost	Alum Cost	Alum Cost per Ton
	Tons	*Tons*	*Tons*				
1927–28	992	552	1421	$17,247	$ 8,019	$ 25,266	$17.80
1928–29	1023	534	1478	13,830	7,270	21,100	14.30
1929–30	1079	550	1518	12,222	7,743	19,965	13.18
1930–31	1693	764	2387	17,824	10,435	28,259	11.80
1931–32	1808	887	2655	18,297	10,150	28,447	10.70
	6595	3287	9459	$79,420	$43,617	$123,037	$13.00

A year's supply has been contracted for, on a basis which will give the following figures:

6595 tons of acid at $9.39 a ton	$62,000
3287 tons of bauxite at $10.72 a ton	35,300
Total cost of amounts used in 5-year period	$97,300

On the basis of 1932 and 1933 yields, it is fair to assume that the 3287 tons of bauxite will yield 9850 tons of aluminum sulfate containing 17 per cent alumina.

Improvement in technic and more rigid specifications have brought about these better yields of alum per ton of ore. The first year only 2.57 tons of sulfate were obtained from a ton of bauxite, whereas the present yield is 3 tons, and often slightly better if excess acid is used.

With changes in grinding, requiring all material to pass a 60-mesh sieve, a 4 per cent increase over present figures should follow. Laboratory tests have demonstrated that this is the increase in yield.

From the above, the cost of 9850 tons of aluminum sulfate is $97,300. The cost per ton on 1932 yield and present prices is $9.88. In order to take care of any slight variation in prices, the figure used in this statement for materials is $10.00 per ton.

MANUFACTURING COST

(Labor only)

UNLOADING A CAR OF BAUXITE

Av. time to unload a 53-ton (117,000-lb.) car, hours	7	
Four laborers at $3.50 a day	$14.00	
One truck, 1 day	1.50	
One truck driver, 1 day	3.20	
Two men in head house, receiving ore	8.00	
Total	$26.70	
Net cost per ton of bauxite	$0.505	
One ton bauxite yields 3 tons 17% alum; net cost per ton of alum, therefore		$0.170

UNLOADING A CAR OF 60° BÉ. ACID

Av. time to unload a 50-ton car, hours	6	
One man to hoop up air line and make occasional inspection, 1/2 day	$2.00	
Cost per ton of acid	0.04	
Two tons of acid are required to make 3 tons of alum; therefore cost per ton of alum will be 2/3 of cost of acid or		0.027

TRANSFERRING BAUXITE TO WEIGHING HOPPERS

(Based on a charge of 12,000 pounds of bauxite and 24,000 pounds of 60° Bé. acid to produce 36,000 pounds of alum)

Three men for 1 hour at $4.00 a day each	$1.50	
Cost per ton of alum produced		0.084

BOILING PROCESS

Two men for 2.5 hours at $4.25 a day each	$2.66	
Alum made, tons	18.0	
Net cost per ton produced		0.150
Total		$0.431

COST OF POWER

UNLOADING BAUXITE

Av. total time to unload 53 tons, hours	7	
Pulverizer motor (1000 kw-hr.) + conveyor motor (640 kw-hr.) = 1640 kw-hr., at 1¢ per kw-hr.	$16.40	
Cost per ton bauxite	0.31	
1 ton bauxite yields 3 tons alum; cost per ton alum = 1/3 of bauxite		$0.10

UNLOADING ACID

Av. total time to unload 50 tons of 60° Bé. acid, hours	6	
25-kw. pump running about 4 hours; 100 kw-hr. at 1¢ per kw-hr.	$1.00	
Cost per ton acid	0.02	
2 tons acid yield 3 tons alum; cost per ton alum = 2/3 acid cost		0.013

TRANSFERRING BAUXITE TO HOPPERS

Av. total time to transfer 12,000 lb., hour	1	
65 kw. for 1 hr. at 1¢ per kw-hr.	$0.65	
Cost per ton of bauxite	0.11	
One ton bauxite yields 3 tons alum; cost per ton alum		0.033

STIRRING ALUM SOLUTIONS WHILE FEEDING

Tons used per day, av. of 5 years	5.5	
One 12-kw. pump runs about 8 hours a day; 12 kw. for 8 hr. at 1¢ per kw-hr.	$0.96	
Cost per ton of sulfate stirred		0.180
Total cost per ton		$0.326

INDIRECT LABOR

Men in head house on alum equipment:

(A) Head operator at	$1900 a year, per day	$ 4.88
(B) Asst. operator at	$1440 a year, per day	3.66
(C) Helper at	$1220 a year, per day	3.05
Total at	$4560 a year, per day	$11.59

Av. tons bauxite received per year (cars)	800 (16)
Av. tons acid received per year (cars)	1600 (35)
Av. tons lime received per year (cars)	2700 (25)
Av. tons alum made per year	2400
Av. batches alum made per year	200

ESTIMATED TIME OF EACH MAN ON ENUMERATED JOB, PER YEAR

MAN	UNLOADING BAUXITE	UNLOADING ACID	UNLOADING LIME	BOILING ALUM	TOTAL TIME
	Days	*Days*	*Days*	*Days*	*Days*
A	16	8	35	32	91
B	16	9	35	32	92
C	0	7	35	60	102
	32	24	105	124	285

Practically one-third of these men's time is taken on the above operations and is accounted for under previous charges. This leaves two-thirds of $4560.00 for maintenance charges on repairs to head house equipment. Handling of lime takes about half of the men's time and must bear its share of the charge. This leaves a charge of one-third of the $4560.00 or $1520.00. Assuming a net yield of alum made on the 5-year basis as 2000 tons, net cost of indirect labor will be $0.76 per ton.

MATERIAL REPLACEMENTS

Total amount of replacements, material costs only	$2000.00
Av. cost per ton of alum	0.21

CAPITAL INVESTMENT IN ALUMINUM SULFATE MANUFACTURING PLANT AND YEARLY DEPRECIATION

ITEM	VALUATION	ESTD. LIFE	DEPRECIATION		TOTAL DEPRECIATION FOR 5 YEARS
		Years	*Value*	*Years*	
Bauxite pulverizer	$ 9,184.76	20	$ 460.00	1	$ 2,300.00
Nash blower and pipe	2,432.27	25	100.00	1	500.00
Bauxite hopper	852.00	25	34.00	1	170.00
Bauxite scales	4,761.91	25	190.00	1	950.00
Screw conveyor	890.00	20	45.00	1	45.00
Screw conveyor	890.00	20	45.00	1	225.00
Boiling tanks	7,841.51	20	392.00	1	1,960.00
Lead linings	4,950.00	5	990.00	1	4,950.00
Acid storage tanks	5,477.47	20	275.00	1	1,375.00
Acid pumps and pipes	1,930.18	5	385.00	1	1,925.00
Air and water piping	2,098.18	10	210.00	1	1,000.00
Acid fume scrubber	1,758.38	10	176.00	1	875.00
Labor on equipment	12,000.00	25	480.00	1	2,400.00
Miscellaneous equipment	754.68	5	150.00	1	750.00
	55,821.34		3932.00		19,425.00
Additional equipment:					
Nash compressor (1930)	606.00	20	30.00	2	60.00
Nash vacuum pump (1931)	3,328.00	20	166.00	1	166.00
Duriron acid pump (1931)	220.00	10	22.00	2	44.00
Duriron acid pump (1932)	422.00	5	84.00	0	0.00
Hoods, tanks 2 & 3 (1931)	860.00	10	86.00	1	86.00
Lead linings 2, 3, 5 (1931)	1,580.00	5	315.00	1	315.00
Acid measuring tank (1932)	75.00	10	8.00	0	0.00
Duriron valves	1,920.00	10	192.00	3	570.00
Pipe line to railway (1931)	2,700.00	10	270.00	1	270.00
Compressor, 4-floor	650.00	25	26.00	0	0.00
	12,361.00		1199.00		1511.00
Total	$68,182.34		$5131.00		$20,936.00

Alum made during 1927 to 1932, tons	9459
Total depreciation	$20,936.00
Net depreciation per ton alum	$2.21

INTEREST ON CAPITAL CHARGES

$55,820 for 5 years at 5%	$13,750.00
1920 for 3 years at 5%	288.00
52 for 2 years at 5%	5.20
837 for 1 year at 5%	41.80
	$14,085.00
Net interest per ton alum	$1.48

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Manufacture, Handling, and Use of Hydrocyanic Acid

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Hydrocyanic acid has been used in the fumigation of citrus trees for control of scale insects since 1886. Until about 1917 hydrocyanic acid was applied by generating the gas in the orchard from sodium and potassium cyanides and sulfuric acid. In 1917 liquid hydrocyanic acid was introduced commercially in California, and within a few years in that state the practice of generating hydrocyanic acid from cyanide and acid in the orchard had been displaced completely by the use of liquid hydrocyanic acid. This paper mentions some of the pertinent properties of liquid hydrocyanic acid, and describes one of the factories in California for making it and the methods of handling and using this material in the orchards.

Hydrocyanic acid is a colorless, mobile liquid with a boiling point of approximately 25.7° C. at 760 mm. and a freezing point of about −14.86° C. (*2*). The specific gravity of anhydrous liquid hydrocyanic acid is 0.682 at 25° C., and of the 97 per cent aqueous solution, used in citrus fumigation, is about 0.692 at 25° C. (*5*). The freezing points of aqueous solutions are as follows:

HCN %	Freezing Temp. ° C.
100	−14.86
90	−21
80	−23
60	−17
40	−16
20	−13
10	− 8

The latent heat of vaporization at the boiling point is approximately 247 gram-calories per gram or about 445 B. t. u. per pound (*2*).

The vapor pressure of hydrocyanic acid has been reported by Sinozako, Hara, and Mitsukuri (*3*), Perry and Porter (*2*), and Bredig and Teichmann (*1*). The vapor pressure curve shown in Figure 1 was plotted from the data of Sinozako, Hara, and Mitsukuri (*3*) because of the temperature range covered. The relatively slight discrepancies in the results from the above three investigations are not regarded as of importance to the chemical engineer.

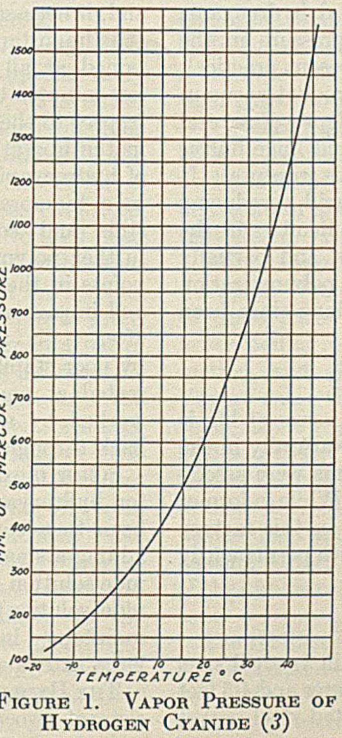

Figure 1. Vapor Pressure of Hydrogen Cyanide (*3*)

Decomposition of Liquid Hydrocyanic Acid

Walker and Eldred (*4*) have described thoroughly the decomposition of liquid hydrocyanic acid. Pure liquid hydrocyanic acid is a very stable substance, but aqueous solutions are less stable. A trace of mineral acids, notably sulfuric, renders aqueous solutions more stable. Any alkaline or alkali-forming substance, added to liquid hydrocyanic acid or its aqueous solutions, greatly accelerates the rate of decomposition. Such substances as ammonia, sodium hydroxide, sodium cyanide, and soap belong to this class while, as noted above, even water renders hydrocyanic acid less stable. Decomposition and polymerization appear to proceed simultaneously, but the combined process is referred to simply as decomposition.

Liquid hydrocyanic acid is normally colorless, and absence of color can be taken as assurance that the liquid is in satisfactory condition at the time of observation. A sample of liquid which eventually decomposes usually remains colorless over an induction period the length of which varies with temperature, pressure, and the nature of any foreign substances which may be in the liquid. The first and unerring indication of decomposition is a faint yellow color which, under ordinary conditions of storage, gradually deepens in intensity, finally passing through yellowish brown, dark brown, and brownish black shades. During the early stages the odor of ammonia frequently can be detected, and in the later stages a black substance is precipitated, the so-called azulmic type of compound, which has substantially the same ultimate analysis as hydrogen cyanide itself and which is referred to here as hydrocyanic acid polymer. Gases are liberated consisting largely of ammonia and carbon monoxide with smaller amounts of nitrogen, oxygen, hydrocarbons, and hydrocyanic acid. Mixed in the hydrocyanic acid polymer can be found also colorless crystals of ammonium cyanide.

The phenomena of decomposition are strongly exothermic and the process is autocatalytic. If the liquid is stored at atmospheric temperature under such conditions that the heat of reaction is completely dissipated by radiation, it is possible for the polymerization reaction to occur almost completely, with little gas formation and little increase of pressure in the container. However, if the heat is incompletely dissipated, the increased temperature may accelerate the decomposition reactions, the process quickly gathers momentum, and the liberated gases may cause a sudden rise of pressure to more than 1000 pounds per square inch with possible rupture of the container. Several cases of such phenomena are reported in the paper by Walker and Eldred (*4*).

Various stabilizers for liquid hydrocyanic acid have been discovered, and many samples of stabilized product have been preserved satisfactorily over periods of a few years. Sulfuric acid to the extent of about 0.005 per cent by weight is the stabilizer commonly used in the factory described here and is quite effective for the conditions encountered in the citrus

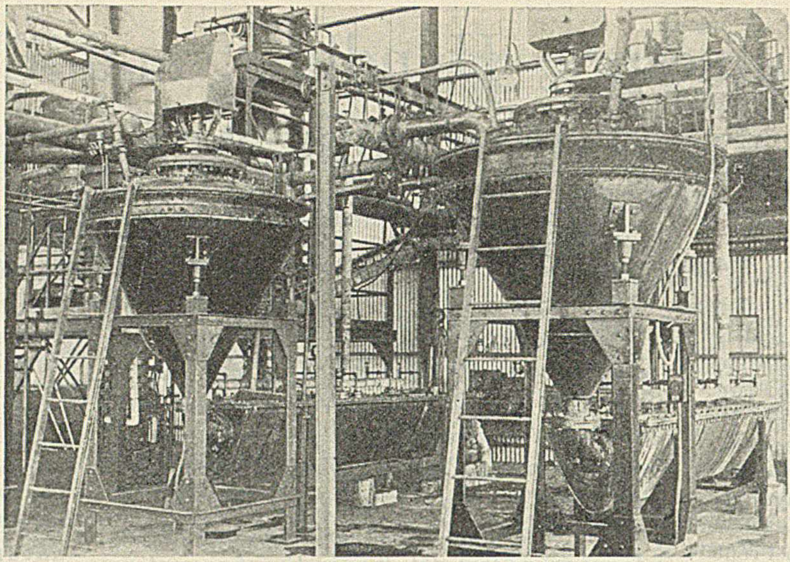

Figure 2. Generator Units

A still is visible in the left background.

fumigation industry of California. Nevertheless, frequent checks are made on the color and acidity of liquid hydrocyanic acid in storage, and any liquid displaying the slightest yellow color is given a protective addition of sulfuric acid and is "reworked" by passing it back through the factory purification process. Traces of alkaline substances are so potent that practically everything used in handling or testing the liquid in the laboratory and plant, after cleaning, is rinsed with sulfuric acid solution. Laboratory glassware is sometimes soaked for hours in acid solution before using, especially if stability tests are involved. In the factory, if a unit is started in operation after a period of idleness, it is first rinsed thoroughly with dilute acid solution. Shipping drums are always washed, inspected internally, tested at 10 to 15 pounds per square inch pressure, and rinsed with dilute acid solution before they are filled.

A peculiarity of polymerized or "decomposed" hydrocyanic acid is introduced by the fact that the volume of the solid, black product formed is greater than that occupied by the original liquid and by the tendency of the black mass to expand in directions of greatest resistance rather than in directions of least resistance. In the laboratory the lower portion of an open glass bottle of decomposed hydrocyanic acid was literally pushed off even though there was ample room for expansion in the upper part of the bottle. In the early days of the factory, in a vertical shell-and-tube condenser in which cooling medium flowed through the tubes and hydrocyanic acid vapor was condensed at atmospheric pressure in the space surrounding the tubes (the reverse of present practice), the black decomposition or polymerization product accumulated on top of the bottom tube sheet to a depth of several inches, and expansion of the material produced huge bulges in the aluminum shell wall and, in some cases, rupture. It also contaminated the liquid hydrocyanic acid, producing off-color and an unstable product. Other difficulties in the shape of plugged pipe lines, condenser tubes, and partially obstructed still plates were caused by the polymerization product. These difficulties, of course, have long since been eliminated.

Toxicity of Hydrocyanic Acid

The toxicity of hydrocyanic acid to most forms of life is too well known to require discussion here. Naturally in the early days of the factory many of the problems were associated with the safety and health of personnel. While in former years operators were occasionally overcome, in this factory not a single man has lost his life or had his health permanently impaired.

The Manufacturing Process

Cyanide Solution. Cyanide is dissolved in vertical steel cylindrical tanks approximately 9 feet in diameter and 4.5 feet high. Each tank is equipped with a perforated steel basket supported 18 inches above the bottom. The basket is approximately 8 feet in diameter. Tank covers are of wood and contain openings for charging the basket with cyanide. The tank is charged with 1250 gallons of water and 5000 pounds of sodium cyanide. Rapid solution is effected by circulation caused by difference between the specific gravities of cyanide solutions and of water. The time required is 2 to 4 hours, depending on the temperature. The solution contains approximately 32 per cent sodium cyanide.

The solution is transferred by a 2-inch, all-iron centrifugal pump to a stock tank where it is diluted with water to a concentration of about 23 per cent sodium cyanide. Mixing is effected by a small mechanical agitator. This solution is pumped to a feed tank from which it flows by gravity through a flowmeter to the hydrocyanic acid generator.

Sulfuric Acid. The 66° Bé. sulfuric acid flows from a steel storage tank to a cast-iron egg and is lifted by air pressure to elevated steel feed tanks. The acid then flows by gravity through a flowmeter to the hydrocyanic acid generator.

The flow of cyanide solution is adjusted to give any desired rate of hydrocyanic acid production. The sulfuric acid flow is adjusted to maintain about 0.5 per cent by weight of free sulfuric acid in the residue or sodium sulfate solution from the generator. Residue samples are tested at frequent intervals for free sulfuric acid and for hydrocyanic acid content, and, if necessary, the rate of flow of sulfuric acid is adjusted. It is important that a slight excess of sulfuric acid be maintained at all times in the generator. If even for only a few minutes there is a slight deficiency of sulfuric acid with respect to the cyanide solution, the alkaline condition results in the liberation of ammonia which induces polymerization of hydrocyanic acid, which, once started, is certain to result in a temporary shutdown for cleaning and acidifying the stills and condensers. Polymerization products catalyze further polymerization of hydrocyanic acid, and at certain points in the stills and condensers the products accumulate and impart a yellowish brown color to the hydrocyanic acid after it is liquefied. Such discoloration is accompanied by poor stability and is a serious matter which must be corrected at once. Discolored hydrocyanic acid must be reworked by acidifying it with sulfuric acid and passing it back through the generators, stills, and condensers.

Sulfur dioxide has been found to be a powerful stabilizer for hydrocyanic acid and the difficulty just described has been to a considerable extent eliminated by the practice of adding a small amount of sodium bisulfite to the sodium cyanide solution (about 4 pounds of bisulfite per batch of cyanide solution). The small percentage of sulfur dioxide thus maintained in the vapors passing through the system has to a large extent eliminated the above difficulty.

The Hydrocyanic Acid Generator. The generator consists of two parts, called, respectively, the mixer and the

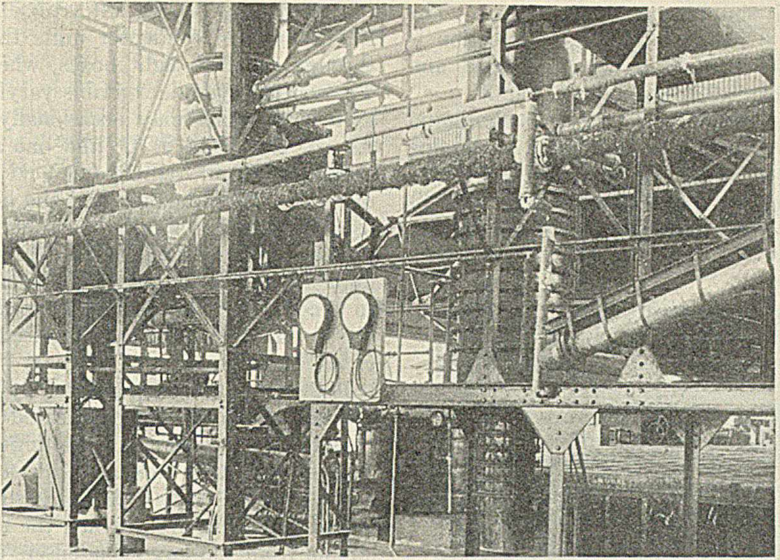

FIGURE 3. STILL, CONDENSERS, DISSOLVED-GAS ELIMINATOR, MIXING TANKS, AND A PORTION OF THE STORAGE SYSTEM FOR HYDROCYANIC ACID

steamer (Figure 2). All internal surfaces are covered with antimonial lead. The mixer consists of a steel funnel whose diameter at the top is 5 feet. The height of the funnel is approximately 4 feet 8 inches, and the diameter of the bottom stem or discharge is 6 inches. The cover contains connections for cyanide and acid solutions, vapor outlet pipes, sight glasses, thermometer well, etc., and also carries a mechanical agitator. Supported near the top of the funnel is a shallow lead mixing basin, 36 inches in diameter and 4.5 inches deep. To the periphery of this basin is secured a lead apron. The vertical shaft of the agitator carries a three-bladed propeller, 20 inches in diameter, which rotates at a speed of 90 r. p. m. in the mixing basin. The cyanide and acid solutions are led through the cover through lead pipes extending to a point just above the propeller and at the middle of the mixing basin. The solutions are mixed very quickly, overflow from the basin and down over the apron, and spill on to the sloping wall of the funnel. Rapid mixing of the cyanide and acid solutions is important since it prevents local overheating and hydrolysis of hydrocyanic acid and makes possible a high hydrocyanic acid recovery efficiency. As the solution flows down the wall of the funnel in a film, about 80 per cent of the hydrocyanic acid is liberated and escapes through a lead vapor outlet pipe. The solution leaves the funnel by way of a 6-inch elbow and flows into the steamer, the function of which is to remove the remainder of the hydrocyanic acid.

The steamer consists of a horizontal, lead-lined, steel trough about 12 feet long whose cross section is approximately that of an equilateral triangle with 2-foot sides. The outlet end is equipped with a discharge connection made adjustable for regulating the depth of liquid to be maintained in the steamer, which usually is 10 inches. The flat cover is equipped with two sight glasses, six thermometer wells, six connections for admitting steam through perforated lead pipes which lie in the bottom of the trough, a 4-inch vapor outlet connection, and near the liquid inlet end an opening for admitting return liquors, which will be referred to later.

Cyanide and acid solutions, as they enter the mixing basin, are joined by a third stream of dilute aqueous hydrocyanic acid solution which consists of liquid from the bottom of the hydrocyanic acid still and solution from a water scrubbing tower to be referred to later. The hydrocyanic acid in these solutions is thus recovered, while the water introduced dilutes the reacting solutions to an extent which avoids difficulty from crystallization of sodium sulfate in the residue solution. The temperature rise in the mixing basin is very rapid and serves to expel about 80 per cent of the hydrocyanic acid as the reacting solutions flow down the wall of the funnel. As the solution then flows through the steamer, the steam is regulated to give a progressively increasing temperature which, at the liquid discharge of the steamer, is about 103° to 104° C. Normally the residue solution contains 0.02 to 0.05 per cent by weight of hydrocyanic acid, corresponding to a loss of about 0.2 to 0.5 per cent referred to the cyanide input. Steam consumption is about 1230 pounds per hour.

The total exposure time of cyanide and acid solutions in the mixer and steamer is about 2.5 minutes. The principle of quick mixing and short exposure time makes it possible to employ 66° Bé. sulfuric acid in this continuous unit with low losses by hydrolysis of hydrocyanic acid at the temperatures involved. The generator is usually operated at a rate of about 650 pounds of hydrocyanic acid per hour but a rate of 800 pounds per hour has been reached at times. This happens to be about the limit of capacity of the still. It is probable that the capacity of the generator is considerably higher, but this has not been determined.

In the remainder of this paper, operating data are based on a production rate af 650 pounds of hydrocyanic acid per hour.

VAPOR SYSTEM PRIOR TO STILLS. All vapor piping from the generator to the stills consists of antimonial lead. The 4-inch vapor pipes from the mixer and steamer enter a 6-inch manifold which carries the vapors to a lead pipe cooler. The latter consists of a vertical bank of five 15-foot lengths of 6-inch pipe connected by return bends. Cooling water trickles downward over the pipes. Vapors enter the cooler at the bottom and leave by the upper pipe. A drain at the inlet to the bottom pipe conducts condensate back to the liquid inlet end of the steamer. Leaving the top of the cooler the enriched hydrocyanic acid vapor enters a separator (where some liquid is separated and returned to the inlet end of the steamer) and then passes to a still.

Neglecting gaseous impurities, vapors entering the cooler at 94° C. consist of about 40 per cent by weight hydrocyanic acid and 60 per cent steam. They leave the cooler at 80° C. and contain about 60 per cent hydrocyanic acid and 40 per cent steam. Cooling water, in summer at 22° C., is used at a rate of approximately 6 gallons per minute.

STILLS. One of the stills is shown in Figure 3. It consists of three parts separated by adapter or spacer sections, a lower boiling or exhausting section, an upper or rectifying section, and above the latter a tubular reflux condenser. Vapors enter the still at about 80° C. and (neglecting noncondensable gases) consist roughly of 60 per cent hydrocyanic acid and 40 per cent steam by weight. The exhauster section below the feed inlet is made of monel metal and is 18 inches in diameter. The boiling section proper in the bottom is 18 inches deep and is equipped with a copper steam coil with heating surface of 11 square feet. Above this are five plates of the bubble cap type, each plate containing ten 3-inch bubble caps.

The rectifier section above the feed consists of seven plates 3 feet in diameter, with twenty-two 4.75-inch aluminum caps per plate. The rectifier section is made up of seven cast-aluminum sections. The bottom of each section forms a plate and the part above it simply consists of a spacer. The height between plates is 6 inches. Each spacer section is fitted with two sight-glass openings on opposite sides, and thermometer wells are included at convenient points.

Mounted directly above the rectifier section is an aluminum reflux condenser 3 feet in diameter × 8 feet high containing two hundred eighty-three No. 16 gage aluminum tubes $1^5/_{16}$ inches o. d. with a cooling surface of approximately 740 square feet. The condenser is capped by a cast-aluminum dome.

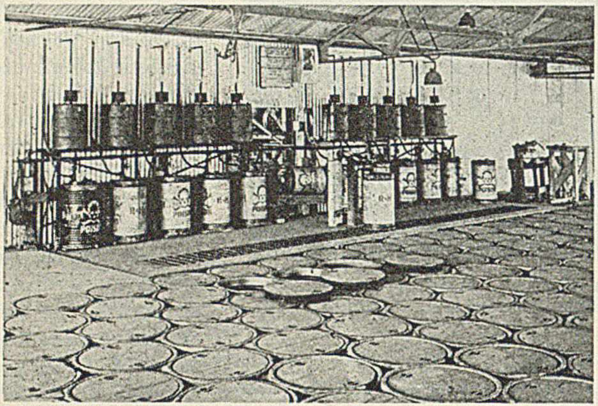

FIGURE 4. DRUM-FILLING STATION AND PART OF STORAGE SYSTEM

The average cooling-water temperature in summer is about 22° C., the rate of flow through the reflux condenser is 150 gallons per minute, and the exit temperature is 25° C. The vapor temperature at the outlet of the reflux condenser is maintained at 32° C., and, when these vapors are liquefied, the liquid consists of 97.5 to 98 per cent by weight hydrocyanic acid. The liquid from the bottom of the still contains only a small percentage of hydrocyanic acid, but, as mentioned before, it is used for diluting the reacting solutions in the generator. The reflux ratio is slightly above 1:1. Steam consumption in the heating coil averages 33 pounds per hour.

Vapors from the reflux condenser pass through 6-inch, welded monel metal piping to the final condensers which consist of two units, the first cooled by water and the second by alcohol brine. All condensers are constructed of aluminum.

The water-cooled condenser might consist of a duplicate of the still reflux condenser. However, simply because the equipment was available, the present unit consists of two tubular exchangers mounted vertically, one above the other, with a 10-inch spacer section between them. Each exchanger consists of a 3-foot diameter shell, 5 feet in length, containing two hundred eighty-three $1^5/_{16}$-inch o. d. No. 16 Stubs gage aluminum tubes. Cooling water at a rate of 90 gallons per minute passes through the exchangers in series, entering at 22° C. and leaving at 25° C. About 30 per cent of the hydrocyanic acid is liquefied in this unit. Vapors pass downward through the tubes and at the lower end pass to the bottom of the brine condenser.

The brine condenser consists of one exchanger similar to those just described. Both vapors and brine enter this unit at the bottom, vapors flowing through the tubes and the brine surrounding them. The brine at a rate of 107 gallons per minute enters at a temperature of $-4.5°$ and leaves at $-3.0°$ C. Vapors escaping the brine condenser pass to a water scrubbing tower where the last traces of hydrocyanic acid are removed. The solution from this tower is added to the still effluent and is used for diluting the reaction mixture in the generator.

DISSOLVED GAS ELIMINATOR. Liquid hydrocyanic acid leaves the two condenser units through 2-inch brass pipes through separate sight boxes, where the color is observed. The sodium cyanide contains varying percentages of sodium carbonate which may occasionally amount to as much as 2.6 per cent. At 0° C. and one atmosphere pressure, one volume of liquid hydrocyanic acid dissolves about eight volumes of carbon dioxide, and the liquid from the condensers usually contains about one volume of carbon dioxide per volume of liquid. In the early days this liquid was drummed immediately, and later, when drums which had been allowed to become very warm were opened, a sudden release of the dissolved gas occurred which caused the drum to behave more or less like a geyser.

Removal of the gas is effected by passing the liquid through a small tubular exchanger, heated with hot water to a temperature barely below the boiling point. The liquid is discharged from this exchanger into a sight box which also acts as a separator. The escaping gas is passed to a small brine-cooled condenser from which the condensate joins the main stream from the large condensers and the gas passes to the water scrubbing tower. The warm liquid is passed through a brine-cooled exchanger and then flows into the mixing tanks.

MIXING TANKS. Liquid hydrocyanic acid is allowed to accumulate in one of these aluminum tanks until approximately 1000 pounds have entered. The concentration is checked by a specific gravity determination, the correct amount of water is added to bring it to the standard shipping concentration of 97 per cent, and about 0.005 per cent by weight of sulfuric acid is added as stabilizer. The solution is thoroughly mixed by means of a 2-inch centrifugal pump. When the concentration is finally adjusted and the batch is approved by the laboratory, the pump transfers the solution to an elevated aluminum tank which serves as a supply for the drum-filling equipment.

DRUM-FILLING STATION. The drum-filling station is shown in Figure 4. The drums are approximately 15 inches in diameter and 26.5 inches in height. They are made of 18-gage steel and are heavily tinned inside and out. The upper head of each drum is equipped with a filling opening, a vent connection (used when the drums are employed on the vaporizing applicators to be described later), and a pressure-relief valve which is set to blow off at 7 pounds gage pressure. Each drum is charged with 100 pounds of 97 per cent hydrocyanic acid. (Recently an 80-pound drum also has been used and a liquid outlet is placed on the side near one end.)

Ten drums are filled at a time. Ten brass measuring tanks are mounted at a convenient height. By means of a manifold and three-way valves, liquid is allowed to flow by gravity from the supply tank upward through the measuring tanks, each of which when full delivers 100 pounds or slightly less. Vent pipes from the measuring tanks are gathered into a header which carries vented vapor from all hydrocyanic acid tanks in the factory to the water scrubbing tower.

Below each measuring tank is mounted at floor level a 3-inch iron roller which operates on the principle of a cam. A guide bar is also mounted at a height of about one foot above the floor. An empty drum, which has been thoroughly washed, slightly acidified with dilute sulfuric acid solution, and tested for leaks, is placed on the roller and against the guide bar under each measuring tank. A motion of a hand-operated lever then causes the roller to lift the drum until the filling opening presses tightly against a rubber gasket on a special fitting attached to the bottom of each three-way valve. When ten drums are placed in position, the three-way valves are adjusted so that the liquid flows from the brass metering tanks into the drums. Any rush of vapor caused by the flow of liquid into the warm drums passes off through vent lines into the common vent-gas header. When the measuring tanks are completely drained, the three-way valves are closed and the drums lowered and closed. They are then passed by means of a roller conveyer at floor level over a scale where they are weighed. They then pass to an automatic topping-off scale where the net weight of hydrocyanic acid is carefully brought up to 100 pounds. The drums are then placed in the storage system.

STORAGE SYSTEM FOR LIQUID HYDROCYANIC ACID. Part of the storage system is shown in Figure 4. Each drum is stored in a separate compartment. Each compartment consists of an 18 × 36 inch tile in a vertical position and with the bell end upward. The storage system was made by placing the tile as close together as possible on leveled ground on which a layer of crushed rock was spread. A 3-inch wood cover fits inside the bell of each tile, resting on the shoulder, and is flush with the upper edge of the tile. The spaces between the tiles are filled with earth to a point about 4 inches from the top, and the remaining space is filled with cement. The tops of the tile, their covers, and the cement, therefore, make a working floor which is flush with the platform of the drum-filling station. In the bottom of each tile is placed a heavy wooden T which supports the drum.

Drums are placed in and removed from the tile by means of a special lifting device which clamps around the drum just below the upper chime. A drum is placed in a special rubber-tired buggy, also equipped with one of the special clamps, and is easily lifted and transported over the top of the storage system to the trucks in which it is shipped to the orchards. This storage system obviously is constructed with the thought of safety uppermost. The system just described has the obvious advantage that only 100 pounds of liquid are stored in each container, and, in case of a bad leak or in case one drum should in some way catch fire, the situation would be more readily controlled. Over a period of about 12 years there has never been a fire or an accident in this storage system.

TRANSPORTATION

The product is delivered to customers by a fleet of trucks equipped with special bodies. These bodies are of steel and wood construction. The side walls extend upward to a height well above the tops of drums but leave a generous space for free circulation of air. A solid partition with a closed window is provided behind the driver's seat. The trucks are driven by experienced and reliable drivers, and the speed is rigidly regulated within specified limits. The driver is always accompanied by an assistant who also is capable of driving. Both are equipped with gas masks and with first-aid equipment. They are thoroughly acquainted with the material which they are handling and are well grounded in a knowledge of the proper procedure in case of emergencies. The drums are loaded into the trucks, one layer deep, a cake of ice is placed on top of each drum and the whole is covered with several thicknesses of canvas. This procedure is especially desirable on some of the longer hauls during the hottest part of the year. There has never been an accident during the transporting of hydrocyanic acid during the 14 years this factory has operated.

Most of the fumigation in California is done by associations and by contracting fumigators. Most of these have special storage rooms where the liquid can be kept cool until it is removed to the orchard for actual use. Deliveries are made frequently so that there is no necessity for storing the liquid in the customer's storage room for more than a day or two.

SPECIFICATIONS OF HYDROCYANIC ACID FOR CITRUS FUMIGATION

The liquid hydrocyanic acid shipped from the factory described herein for citrus fumigation is of the following quality:

	SPECIFICATION	ACTUAL TESTS
Color	Water white	Water white
Concentration, % HCN	96.5–97.5	Not less than 97
Free H_2SO_4, %	Not over 0.01	About 0.005
Dissolved vol. gas per vol. liquid	Not over 0.25	About 0.15

The hydrocyanic acid concentration of the product is checked in the field at frequent intervals by county and state inspectors. The determination involves only a measurement of the specific gravity and temperature, and reference to a chart such as that given by Walker and Marvin (*5*).

FUMIGATION OF CITRUS TREES

Hydrocyanic acid is used for control of scale insects. In Southern California the principal scale insects controlled by fumigation are the black, red, purple, and citricola scales. Because of the necessity for fumigating at the proper stage in the life cycle of the insect, because of calendar differences in the life cycles of the above varieties, and because of different climatic conditions in different localities, fumigation, while seasonal in each locality, is being conducted over a major part of the year in some part of the citrus belt. The least active season is from April 1 to July 1; the most active season from July 1 to December 1.

FIGURE 5. A ROW OF TREES BEING FUMIGATED WITH A VAPORIZER

Most fumigation is performed at night since there is much less danger of injury to the tree. In fumigating a tree, a canvas tent is pulled over the tree and liquid hydrocyanic acid is applied to the space under the tent in carefully measured dosages. The tent is then allowed to remain on the tree for about 45 to 60 minutes. The hydrocyanic acid is applied in two ways, by atomizing the liquid and by vaporizing it. Atomizing applicators are known as pumps, and vaporizing applicators as vaporizers.

The atomizer or pump is carried by hand through the orchard by a member of the crew, known as the gun man. It consists essentially of a 3- or 4-gallon tank, a very accurate liquid-measuring device, and a pump for forcing the measured charge of liquid through a short delivery pipe to an atomizing nozzle which is thrust under the canvas wall of the tent. The tents are marked with a scale which measures the tents from the ground up over the top of the tree and down to the ground on the other side. A member of the crew known as the taper quickly measures the distance around the tent and, by consulting a chart which he carries announces the correct dosage. The proper amount of liquid hydrocyanic acid is then atomized under the tent. The nozzle is designed to give an exceedingly fine, misty spray which results in almost instantaneous evaporation of the liquid. This is important since contact of liquid hydrocyanic acid with foliage burns the latter severely, and also because it is desirable to produce as quickly as possible the maximum concentration of hydrocyanic gas in the tented space. The above method is satisfactory during the warmer part of the season. However, on cool nights when hydrocyanic acid is evaporated less quickly, there is a tendency for some liquid to fall to the ground or to condense on the ground or on the lower foliage of the tree or on cover crops which may be growing in the orchard. For these reasons the vaporizer is used to a large and increasing extent.

The vaporizer is drawn through the orchard by a horse or may be motor-mounted. This is a two-wheeled, rubber-tired vehicle on which are mounted a water boiler heated by an oil burner with the necessary small oil supply tank and connections. The water boiler contains a copper coil which acts as a vaporizer for the liquid hydrocyanic acid. At a convenient point is mounted a measuring device somewhat similar to that on the atomizing machines. Provision is made for placing two 100-pound shipping drums of liquid hydrocyanic acid on the vehicle and for connecting them to the measuring pump. The latter forces the liquid through the copper coil in the water boiler where it is converted almost instantaneously into a warm vapor which then passes through a length of special, flexible hose which is placed under the edge of the tent. The boiler is operated at a pressure of 20 pounds gage, and, after a tree has been "shot," the hose is flushed out with a small amount of steam from the boiler before being withdrawn from under the tent. This is to prevent unnecessary exposure to hydrocyanic acid escaping slowly from the hose while the vaporizer is being taken from tree to tree. Figure 5 shows a row of trees being fumigated with a vaporizer.

ACKNOWLEDGMENT

Acknowledgment is made to the following men of the Pacific R. & H. Chemical Corporation: F. S. Pratt for his many helpful suggestions, D. N. Eldred for much of the data used, and C. J. Marvin for the photographs.

LITERATURE CITED

(1) Bredig and Teichmann, *Z. Elektrochem.*, 31, 449-54 (1925).
(2) Perry, J. H., and Porter, Frank, *J. Am. Chem. Soc.*, 48, 299 (1926).
(3) Sinozako, H., Hara, R., and Mitsukuri, S.. *Bull. Chem. Soc. Japan*, 1, 59 (1926).
(4) Walker, Mark, and Eldred, D. N., IND. ENG. CHEM., 17, 1074 (1925).
(5) Walker, Mark, and Marvin, C. J., *Ibid.*, 18, 139 (1926).

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Rotary Vacuum Filtration of Crystal Sugar

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A theoretical method for determining the efficiency of the rotary vacuum filter in the purging of crystal sugar is given.

DURING the past few years there has been considerable investigation to determine the suitability of the rotary vacuum filter for the purging of crystal sugar. This investigation has taken the form of actual operation tests and, although the data obtained have indicated that the use of the rotary vacuum filter in the purging of sugar might be feasible in all but the lowest grades, no installations for this purpose have as yet been made. However, the possibilities of the rotary vacuum filter in this field have not so far been thoroughly determined, owing mainly to the complicated nature of the factors determining the efficiency of the process and also to the high cost of actual operation tests.

In this article the subject is treated theoretically by use of a schematic procedure which illustrates the actions occurring throughout various stage systems with countercurrent washing. By use of the schematic procedure given, actual results may be determined for the processing by rotary vacuum filtration of any given massecuite under given operating conditions with the aid of washing data secured from laboratory tests.

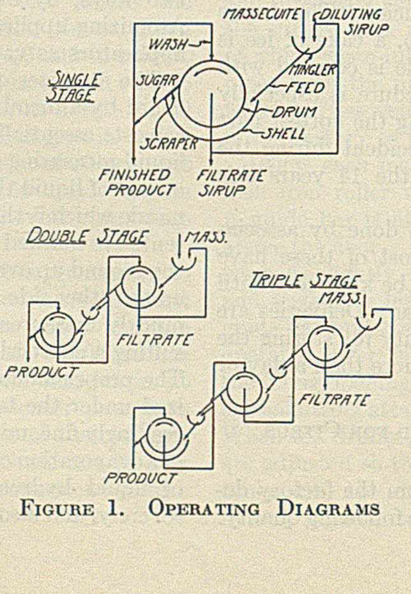

FIGURE 1. OPERATING DIAGRAMS

OPERATING EFFICIENCY

In the purging of crystal sugar from its massecuite, the efficiency of the operation is determined by (1) the finished product purity and (2) the yield. The purity of a sucrose-containing substance is the ratio of the sucrose to the total solids; the yield is a measure of the efficiency in the sucrose extraction process and may be expressed in several different manners. In this work yield is expressed as pounds of sucrose in finished product per 100 pounds of massecuite solids.

In any type of filtration process the purity of the finished sugar may be raised to practically any desired value but at the expense of the yield. This is evident from the fact that an increase in washing, either by water or high-purity sirup, raises the finished product purity and lowers the yield. By use of the rotary vacuum filter in series with countercurrent washing, the question arises as to the optimum number of filters to be used; for, the greater the number, the greater will be the resultant efficiency in purging. However, in increasing the number of stages, the increase in purging efficiency for each succeeding stage grows less; and as the number of stages is increased indefinitely, there is a maximum value for the purging efficiency which is approached. In this article the relative magnitudes of purging efficiency for various stage performance are illustrated by yield *vs.* purity curves in various and infinite stage operation for a typical low-grade sugar under typical operating conditions.

The general operating scheme applicable for rotary vacuum filtration of crystal sugar is shown in Figure 1. In operation, as illustrated in the single-stage diagram, the massecuite flows first into a mingler where it is diluted with part of the filtrate sirup to lower its consistency and to give good workability. The use of this sirup as a diluent also gives greater efficiency in operation owing to a quantity of higher purity wash liquor going through the cake and subsequently raising the purity of the mixed liquor in the feed. The greater the amount of this recirculated sirup used, the greater will be the purging efficiency; however, as the amount is raised, the beneficial effect of each succeeding amount grows less so that it is practical to use only approximately the same weight of recirculated solids as massecuite solids. This gives a feed of good workability and the beneficial effect of using more diluting liquor is too small to be of any consequence. As the drum rotates, the section immersed in the feed contained in the shell is coated with sucrose crystals as the feed liquor is drawn through the drum screen by vacuum. When any given portion of the sucrose cake reaches the wash at top of drum, the excess liquor has been drained off and that remaining is determined by the temperature and moisture content and is dependent upon a large number of complicated factors, most of which are dependent upon the properties of the massecuite. As the sugar passes under the wash, which here is taken as a saturated solution of the finished product, the liquor in the cake is displaced in a complex manner by the wash liquor to a degree varying with the amount of wash used. It is by varying the amount of this wash liquor that the yield *vs.* purity curve may be established for a given set of conditions.

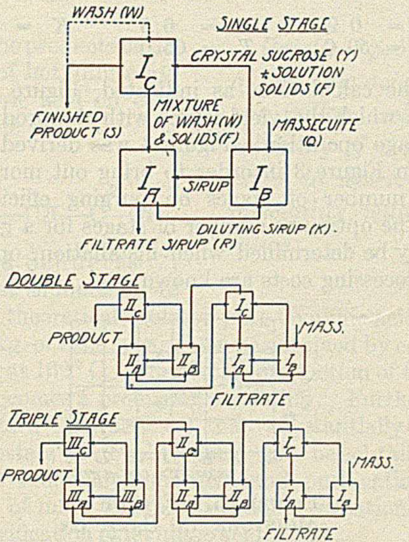

FIGURE 2. SOLIDS FLOW DIAGRAMS

In obtaining the yield *vs.* product purity curve for a massecuite of any given characteristics, the method used involves the establishing of simultaneous equations throughout the system in order to tie up the numerous factors affecting operation. The properties of the massecuite are then substituted into the equations along with certain operating characteristics as desired and others determined by laboratory test data.

FACTORS DETERMINING OPERATION

The factors determining operation may be broken up into two classes: (I) massecuite characteristics and (II) operation characteristics. Under massecuite characteristics the factors are: (1) purity of massecuite, (2) percentage sucrose crystals, (3) temperature, and (4) character of sucrose crystals. Under operation characteristics the factors are: (1) amount of sirup recirculated, (2) temperatures in system, (3) amount of wash used, (4) moisture in sugar cake after drainage, and (5) percentage of total wash used that remains in cake after drainage. Strictly speaking, the moisture in cake after drainage and the percentage wash remaining after drainage are, in part, functions of the massecuite characteristics. However, since these two factors are dependent upon numerous complex fundamental factors, it is much more logical to term them operation characteristics and to determine their values by laboratory test data. For use in the simultaneous equations the nomenclature is as follows on a basis of 100 pounds of massecuite solids:

P = purity of substance, sucrose/total solids
Y = sucrose crystals in mass, % of total solids
M = moisture in sugar cake after drainage, %
K = sirup solids recirculated, lb.
T = temp. of sugar cake, ° C.
E = wash solids remaining in cake, % of total
F = dissolved solids in cake after drainage, lb.
W = wash solids, lb.
Q = massecuite solids, 100 lb.
R = filtrate sirup solids, lb.
S = finished product solids, lb.

The factor F, denoting the dissolved solids in the sugar cake on drum after drainage, is a function of the percentage sucrose crystals (Y) and of the temperature (T) and moisture (M) of the sugar cake. For a temperature range of 50° to 70° C. the following relation holds true very closely for pure sucrose solutions and is used in the calculations of this work with negligible error:

$$F = (Y)\left(\frac{0.075 + 0.0447T}{\frac{100}{M} - 1.075 - 0.0447T}\right)$$

Factor E, denoting percentage of total wash solids remaining in cake after drainage, must be determined by laboratory test data. To determine accurately the characteristics of processing crystal sugar by the rotary vacuum filter, the effect of grain and liquor characteristics on factor E must be established. This has not as yet been attempted. In establishing E for use in obtaining the graphs in this article, the following empirical equation was devised from test data on typical low-grade sugar:

$$E = \left(\frac{F}{W}\right)\left(1 - \frac{1}{\left(\frac{W}{F} + 1\right)^{\frac{W}{F} + 1}}\right)(100)$$

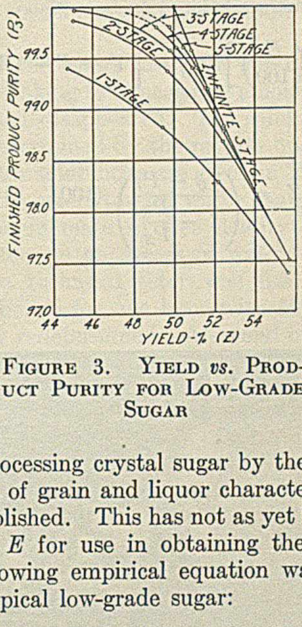

FIGURE 3. YIELD *vs.* PRODUCT PURITY FOR LOW-GRADE SUGAR

In order to obtain a clear conception of the actions occurring throughout a given system, the solids flow diagrams (Figure 2) are used. These diagrams also furnish a basis on which to establish the necessary simultaneous equations. The various parts of Figure 2 represent sections of the systems wherein changes in purity of liquor are taking place. Section A shows the inside of the drum; section B gives the mingler and shell portion of the system; and section C represents that portion of the system undergoing washing.

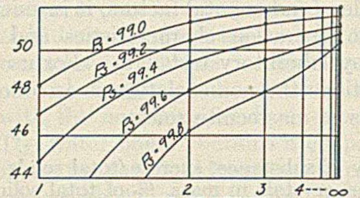

Figure 4. Effect of Number of Stages on Yield

For establishing the relations among the various factors in n = stage performance, simultaneous equations are obtained from the following:

1. Sucrose balance on section A in each stage
2. Sucrose balance on section B in each stage
3. Sucrose balance on section C in nth stage

In illustration of the equations used to determine the finished product purity (P_S) and the filtrate sirup purity (P_R) from which the yield (Z) is calculated, the following are those used in single stage:

Derived from sucrose balance on I_A,

$$\left[K + Q - Y - F + (W)\left(\frac{E}{100}\right)\right]P_{I_B} + (W)\left(\frac{100 - E}{100}\right)P_S = (K + Q + W - Y - F)P_R \quad (1)$$

Derived from sucrose balance on I_B,

$$QP_Q + KP_R = Y + (K + Q - Y)P_{I_B} \quad (2)$$

Derived from sucrose balance on I_C

$$Y + \left[F - (W)\left(\frac{E}{100}\right)\right]P_{I_B} = \left[Y + F - (W)\left(\frac{E}{100}\right)\right]P_S \quad (3)$$

Yield formula,

$$Z = \left(\frac{P_Q - P_R}{1 - \frac{P_R}{P_S}}\right)(100) \quad (4)$$

In these formulas purity (P) is in the fractional form and the subscripts denote the substance under consideration either directly or indirectly. In illustration, the symbol P_S denotes the purity of the finished product, and the symbol P_{I_B} denotes the purity of the liquor leaving the section I_B.

In applying the foregoing procedure to determine the effect of number of stages on the purging efficiency, the following typical massecuite and operation characteristics are assumed and the wash (W) is varied for various stage operations:

$$P_Q = 0.90 \qquad M = 6.5 \qquad K = 100.0$$
$$Y = 50.0 \qquad T = 65.0$$

From the calculations as indicated, Figure 3 shows the manner in which the yield varies with the product purity in various stage operation. Figure 4 was derived from values taken from Figure 3 in order to bring out more clearly the effect of number of stages on purging efficiency. From Figure 4 the optimum number of stages for a given product purity may be determined when installation, operation, and sugar reprocessing costs are known.

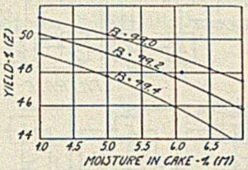

Figure 5. Effect of Moisture in Cake on Yield for Single Stage

Another application of the theory given is the determination of the effect of moisture in cake after drainage on the yield for a given product purity. This was calculated and is illustrated in Figure 5 for single-stage operation. These curves are of particular interest as they illustrate the effect of varying drainage (as determined by the cake moisture content) on the yield, other factors remaining constant; and, while drainage is the greatest problem in the use of the rotary vacuum filter on crystal sugar, there are no specific data on the effect of the fundamental factors determining the degree of drainage.

In rendering this theoretical treatise, the author believes that the schematic procedure given can be used to advantage in any future investigations to determine the feasibility of the rotary vacuum filter or similar equipment in the processing of crystal sugar.

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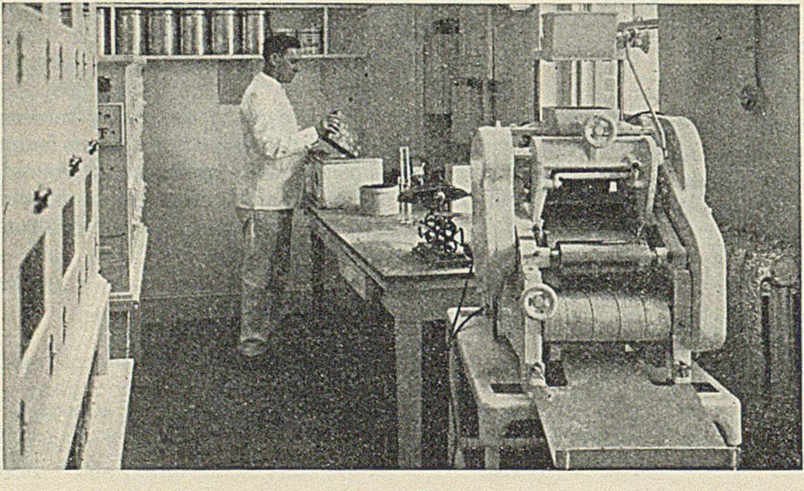

Baking Laboratory, Bureau of Agricultural Economics, U. S. Department of Agriculture

Industrial Uses for Cane Sugar

II. Properties of Alkyl Esters of Levulinic Acid[1]

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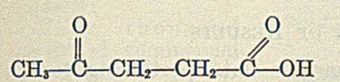
Multiple Fellowship of the Sugar Institute, Inc., at Mellon Institute of Industrial Research, Pittsburgh, Pa.

Practical properties of thirteen aliphatic esters of levulinic acid are given: boiling point, weight per gallon, solubility of the esters in water, solubility of water in the esters, stability of the esters to water, solubility of gums and resins, miscibility with organic solvents, and dilution ratios.

ONE of the products of the action of hot, dilute hydrochloric acid on cane sugar is levulinic acid,



$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{/\!/}{C}}-OH$

As Thomas and Schuette (*7*) have shown that as much as 42 per cent of the theoretical yield of pure levulinic acid—i. e., 285 grams per kg. of cane sugar—can be obtained by conducting the reaction at 162° C., commercial production of the acid and its esters becomes a promising possibility. Furthermore, it has been shown elsewhere (*2*) that substantially higher yields of the esters of levulinic acid can be obtained by esterification of crude levulinic acid and purification than by a succession of more tedious operations—isolation, purification, and esterification of levulinic acid.

The reaction of sucrose and hydrochloric acid yields, in addition, formic acid equivalent to the levulinic acid and about 22 per cent of the original weight of the sugar as the so-called artificial humic acid. Recovery and utilization of these by-products are essential to commercialization of the levulinic acid reaction.

Some of the difficulties which lie in the path of development of levulinic acid production are the still comparatively low yield of the acid, difficulties in distillation owing both to high boiling points and to the accumulation of "tars," and the corrosive action of the mixtures at the high temperatures and pressures necessary for the reaction.

Recent reports on levulinic acid esters have been those of Sah and Ma (*5*), Schuette and Cowley (*6*), Cowley and Schuette (*1*), and Cox and Dodds (*2*). Authors to date have concerned themselves with the physical and chemical constants of the esters and not with useful applications. The objective has been the development of uses for these esters and, as means to that end, certain practical properties of the levulinic esters have been examined.

The esters studied are twelve in number, as described in another paper (*2*), and the mixed esters derived from esterification of Pentasol,[2] a commercial mixture of amyl alcohols. The data given in the communication dealing with the preparation of these esters (*2*) are vapor pressure, boiling point, specific gravity, surface tension, and index of refraction. Herein are given data of solubility relations to water, organic solvents, and resins, of stability of the esters to water, and also some general observations.

PROPERTIES OF ESTERS OF LEVULINIC ACID

The alkyl esters of levulinic acid, up to the hexyl series, are colorless liquids boiling in the range 196.0° (methyl) to 253.4° C. (*N*-amyl). The lower esters (methyl, ethyl, and propyl) have pleasing melon-like odors; the butyl and amyl series have only faint, but still pleasant odors. The taste of the esters is intensely burning and bitter. The boiling points shown in Table I are those observed by Cox and Dodds (*2*) in the vapor pressure apparatus of Ramsay and Young (*4*) at exactly 760 mm. pressure. The boiling point of the mixed amyl levulinate was determined in the same way.

The indexes of refraction (Table I) are those given by Cox and Dodds (*2*). The weights per gallon of the esters are derived from the specific gravities reported in the same paper.

The solubility of the esters in water was determined by adding water with shaking to a measured amount of the ester until opalescence just disappeared. The solubility of water in the esters was determined by the reverse operation. The data relating to water solubilities are given in Table I.

The stability of the esters toward water has been observed by determining the increase in free acidity produced by exposure of the esters to an excess of water. Specifically, free acidity in the technical ester was first determined. Then one cc. was boiled for one hour with 50 cc. of water and the free acidity redetermined. A second one-cc. sample was heated for 5 days at 40° C., and the increase in free

TABLE I. PHYSICAL AND CHEMICAL PROPERTIES OF ALKYL LEVULINATES

ALKYL LEVULINATE	B. P. AT 760 MM. Hg (OBSD.)	INDEX OF REFRACTION AT 20° C	SP. GR., 20°/4° C.	WT. PER GAL.	SOLUBILITY		STABILITY TO WATER		
					Ester in water	Water in ester	INITIAL ACIDITY	ACIDITY AFTER: Boiling for one hr.	5 days at 40° C.
	° C.			*Lb.*	*Cc. per 100 cc.*		%	%	%
Methyl	196.0	1.42333	1.0495	8.74	Completely miscible		5.7	7.4	7.9
Ethyl	205.8	1.42288	1.0111	8.42	12.5	7.5	2.6	4.3	6.0
N-propyl	221.2	1.42576	0.9896	8.24	2.8	3.4	0.2	0.9	0.9
Isopropyl	209.3	1.42088	0.9782	8.15	5.9	3.6	0.5	1.2	1.1
N-butyl	237.8	1.42905	0.9735	8.11	0.93	2.12	0.9	1.6	2.0
Isobutyl	230.9	1.42677	0.9677	8.06	1.2	2.06	1.5	2.8	2.9
sec–Butyl	225.8	1.42499	0.9670	8.06	1.6	2.06	2.3	2.9	3.2
N-amyl	253.4	1.43192	0.9614	8.01	0.26	1.45	0.4	1.0	1.0
Isoamyl	248.8	1.43102	0.9603	8.00	0.25	0.99	0.6	1.2	1.0
Methylpropylcarbinol	239.6	1.42808	0.9557	7.96	0.40	0.79	3.1	3.3	3.3
Diethylcarbinol	239.0	1.42890	0.9591	7.99	0.50	0.55	3.5	3.7	3.7
2-Methylbutyl	247.2	1.43100	0.9607	8.00	0.30	1.12	0.4	0.9	1.1
Mixed amyl	246 (approx.)	.....	0.9589	7.99	0.29	0.89	0.8	1.2	1.2

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[1] The first paper of this series appeared in IND. ENG. CHEM., News Ed., 10, 149 (1932).

[2] Pentasol and alcohols of the amyl series were supplied by the Sharples Solvents Corporation.

acidity measured. These data of initial free acidity and also the results of hydrolysis at 100° and at 40° C. are shown in Table I.

The qualitative solubilities of some resins and gums in levulinic acid esters have been observed by treating approximately 0.5 gram of the substance with the 5-cc. portions of the esters. As these solubilities are similar for each group of isomers, the esters (Table II) are grouped in their respective series—methyl, ethyl, the propyl (C_3), butyl (C_4), and amyl (C_5) esters.

TABLE II. QUALITATIVE SOLUBILITY OF COMMERCIAL GUMS AND RESINS IN THE ESTERS OF LEVULINIC ACID

RESIN	METHYL[a]	ETHYL	C_3	C_4	C_5
x-Manila	–	–	–	×	×
Montol	×	+	+	+	+
Kauri	×	×	–	×	×
Pontianac chips	×	×	–	–	–
Rosin	+	+	+	+	+
Bone-dry shellac	–	–	–	–	–
Bakelite (viscous)	Gels	Gels	+	+	+
Rezyl	–	+	+	+	+
Sarpee	–	–	–	–	–
Ester gum, unoxidized	+	+	+	+	+
Ester gum, oxidized	×	+	+	+	+
Albertol copal	×	+	+	+	+
Albertol	×	+	+	+	+
Amberol	×	×	+	+	+
Cumar	+	+	+	+	+
Dammar	–	–	–	–	×
Varnish type glyptal	+	+	+	×	+
Vinylite 80	Gels	Gels	Gels	Gels	Gels
Urea formaldehyde	–	–	–	–	–

[a] + = completely soluble; – = insoluble; × = partially soluble.

In general, it was found that the esters are completely miscible with the simple alcohols, immiscible with ethylene glycol and glycerol, and miscible with ethers, aldehydes, ketones, esters, acids, chlorinated aliphatic hydrocarbons, aromatic hydrocarbons, the Cellosolve group, and fatty oils. Methyl levulinate differs from the above generalization in being completely miscible with ethylene glycol and immiscible with fatty oils. Ethyl levulinate is also immiscible with ethylene glycol.

The tolerance of levulinic acid ester solutions of 1/2 second nitrocellulose for dilution with (1) toluene, (2) *N*-butyl alcohol, and (3) Kemsoline (a commercial petroleum-distillate diluent) have been determined by the Hercules Powder Company's method for dilution ratios (*3*). These data are given in Table III.

TABLE III. DILUTION RATIOS OF SOLUTIONS OF 1/2 SECOND NITROCELLULOSE

ALKYL LEVULINATE	TOLUENE		BUTYL ALCOHOL		KEMSOLINE	
	Diln. ratio	% Nitrocellulose	Diln. ratio	% Nitrocellulose	Diln. ratio	% Nitrocellulose
Methyl	2.40	7.8	2.35	8.2	Immiscible	
Ethyl	2.85	7.2	3.25	7.4	0.45	6.9
N-propyl	3.00	7.3	3.85	8.0	0.75	5.9
Isopropyl	2.80	7.8	5.05	6.1	0.60	6.3
N-butyl	3.15	7.7	6.40	6.4	1.0	5.3
Isobutyl	2.95	8.0	6.00	6.8	0.85	5.6
sec-Butyl	2.75	7.7	5.55	6.5	0.85	5.7
N-amyl	3.25	7.4	7.50	7.2	1.15	5.1
Isoamyl	3.00	8.2	7.50	7.6	1.0	5.3
Methylpropylcarbinol	2.80	9.7	7.75	6.5	0.93	5.5
Diethylcarbinol	3.10	7.9	8.00	6.5	0.85	5.6
2-Methylbutyl	3.00	8.0	7.85	7.5	1.0	5.3
Mixed amyl	2.80	8.0	7.25	7.5	1.1	5.0

DISCUSSION OF RESULTS

An examination of the various data pertaining to the properties of the esters of levulinic acid reveals that the better characteristics for most present commercial uses of such materials are found in the members of the butyl and amyl series. Generally these esters are more stable toward water, have lower solubility relations to water, and better dilution ratios of nitrocellulose solutions than the lower homologs. Their solvent powers seem to be as good as those of the lower esters.

LITERATURE CITED

(1) Cowley and Schuette, *J. Am. Chem. Soc.*, **55**, 387 (1933).
(2) Cox and Dodds, *Ibid.*, **55**, 3391 (1933).
(3) Gardner, "Physical and Chemical Examination of Paints, Varnishes, Lacquers, Color," 5th ed., p. 730, Institute of Paint and Varnish Research, Washington, 1930.
(4) Ramsay and Young, *J. Chem. Soc.*, **47**, 42 (1885).
(5) Sah and Ma, *J. Am. Chem. Soc.*, **52**, 4880 (1930).
(6) Schuette and Cowley, *Ibid.*, **53**, 3485 (1931).
(7) Thomas and Schuette, *Ibid.*, **53**, 2324 (1931).

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III. Technology of Sucrose Octaäcetate and Homologous Esters

GERALD J. COX, JOHN H. FERGUSON, AND MARY L. DODDS

A simplified convenient method for the preparation of sucrose octaäcetate in high yield is described, together with analogous processes for making sucrose octapropionate and sucrose octabutyrate. Properties of value in the industrial application of these esters of sucrose are given.

THE fact that sucrose has been considered primarily as a food, condiment, or confection by the layman, or as an example of an abundant disaccharide by the chemist, has in most cases far overshadowed its possible use as a polyhydric alcohol. The production of esters from this compound, utilizing as it does these same alcoholic properties, therefore seemed to offer a starting point for the development of a group of industrially useful organic products.

The comparatively low cost and high available tonnage of sucrose obtainable in such a high state of purity as is commonly found upon the consumer's table also contributed to the belief that such a source material or some of its derivatives could be used both extensively and advantageously in industrial processes.

With this idea in mind, and cognizant of the extensive commercial use of the esters of allied substances—for example, cellulose acetate—the lower saturated aliphatic acids were considered as possible reactants for the production of similar compounds of sucrose.

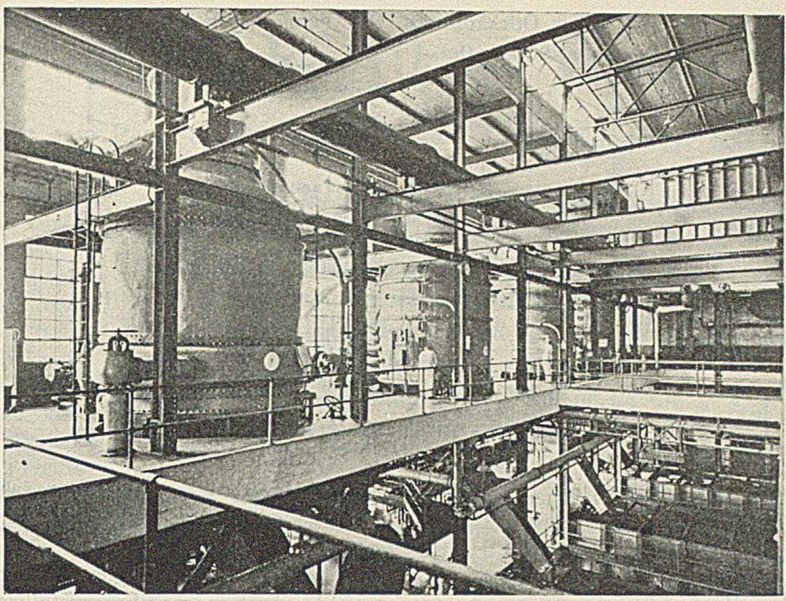
The investigation to be reported, therefore, is concerned with some of the phases of production of the most promising member of the series—i. e., sucrose octaäcetate—together with the properties that might apply commercially to its use. Mention is also made of the properties of the two next highest members of the homologous series—i. e., sucrose octapropionate and sucrose octabutyrate.

Schutzenberger (*3*) was the first to acetylate sucrose but was able to obtain only a gummy mass from the process. Later Herzfeld (*1*) was able to obtain a crystalline product and likewise listed some of its physical characteristics. The octapropionate and octabutyrate are new compounds.

SUCROSE OCTAÄCETATE

LARGE-SCALE LABORATORY PRODUCTION IN GLASS. The preparation of sucrose octaäcetate in 6- to 8-pound lots was carried out, using the apparatus shown in Figure 1.

The Liebig condenser, *A*, is ground into the neck of a 12-liter balloon flask, *B*. Through the 2-inch (5-cm.) condenser runs sleeve *C*, carrying stirrer *D* turned by motor *E* through the rubber-tube universal joint, *F*. The sleeve is made of heavy glass (4-mm. wall), braced at *G* with three glass points, and supported at *H* by a clamp and rubber stopper. The flask is heated by oil bath *J* and electric plate *K*.



Refinery Pan Floor

Four thousand grams of commercial acetic anhydride (90 per cent) and 150 grams of freshly fused sodium acetate were placed in the 12-liter flask and heated to boiling with stirring (145° C. oil-bath temperature). The electric plate was shut off as the reaction was rapid and exothermic. Fifteen hundred grams of granulated sucrose were added down the condenser at the rate of about 100 grams per minute. After all the sucrose had been added, the electric plate was again turned on to continue rapid boiling of the reaction mixture. More acetic anhydride (500 grams) was poured down the condenser to wash into the reaction vessel any sucrose that had adhered to the sides. Boiling of the mixture was then continued for 10 minutes and the current again shut off. When refluxing ceased (in about 15 minutes) the solution was heated with 75 grams of decolorizing carbon (Nuchar) and filtered while hot into a 12-liter flask. The solution was evaporated *in vacuo* in a boiling water bath until the distillate came over only in occasional drops. The hot sirup was poured into about 12 liters of tap water contained in a 24-liter stoneware jar and stirred vigorously with a heavy paddle. The water was poured off and renewed, and stirring was continued until the sucrose acetate became a stiff mass. By allowing this mass to stand overnight in water, it became crystalline.

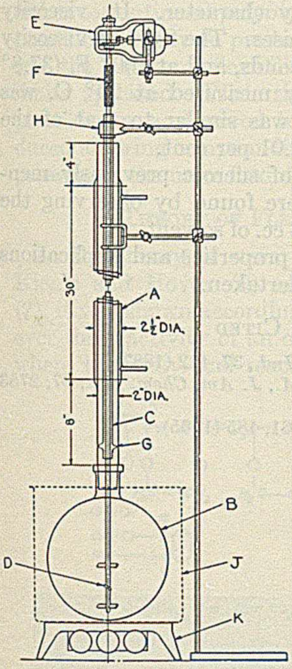


Figure 1. Apparatus for Preparation of Sucrose Octaäcetate

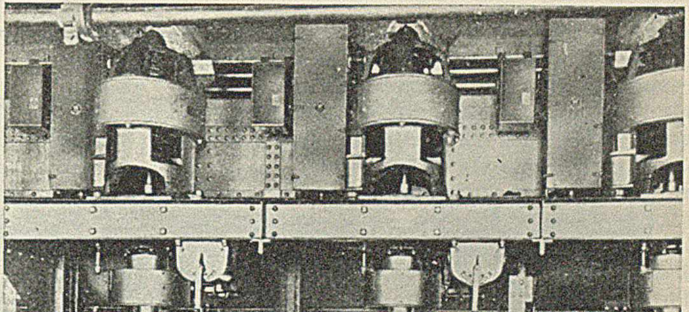
After the crystallization, the water was poured off and the hard mass was broken and ground in a mortar. It was then washed with tap water on a 12-inch (30.5-cm.) stoneware vacuum filter until the washings were entirely neutral to litmus paper. The final product was then dried in air.

The yield secured in this process was 2600 to 2730 grams, or 88 to 92 per cent of theoretical.

Semi-Plant Production. The compound was also made successfully on a semi-plant scale, using a copper still of 20 gallons capacity. The amounts of reactants were proportionately the same as those used in the laboratory production. The working up of the product, however, was slightly different. After the reaction was complete and after the distillation of acetic acid had been made, the sirup was dissolved in toluene and heated to boiling with solid hydrated lime. All free acid was completely neutralized by this method before the boiling point of the solution was attained. The mixture filtered readily, and practically all the color was retained in the residue, leaving the toluene solution a very light amber color. It is possible either to use this solution directly in order to incorporate the compound into other materials of a resinous nature, or by concentration of the toluene solution to crystallize and use the acetate as a solid. Although the acetate is of crystalline form, it was found to change into a clear, transparent, colorless glass after fusion and cooling. This property alone suggests its use in plastics, resins, and like materials, together with a variety of possible combinations in various specialized commercial processes.

The melting point of the crystalline solid was found to be 68° to 69° C., although the observation varied considerably with the rate of heating, owing to the high viscosity of the compound at its melting point. Decomposition and subsequent charring occurred at about 285° C., but the compound has been distilled unchanged at 260° C. in the vacuum produced by a Cenco Hyvac oil pump. The density using the glasslike resinous form was found to be 1.28 at 20° C. Its viscosity at 100.2° C. was equal to 29.54 poises.

A sample of the product was recrystallized from alcohol five times and its optical rotation measured in chloroform. The average result was $[\alpha]^{24}_{\mathrm{D}} = +59.79°$. In comparison to this result is the value $[\alpha]^{20}_{\mathrm{D}} = +59.6°$, given by Hudson



Centrifugal Machines

TABLE I. SOLUBILITIES OF SUCROSE OCTAÄCETATE, OCTAPROPIONATE, AND OCTABUTYRATE AT 25° C.

SOLVENTS	SUCROSE OCTAACETATE[a]	SUCROSE OCTAPROPIONATE	SUCROSE OCTABUTYRATE
Methyl alcohol	+	+	+
Ethyl alcohol	+	+	+
Butyl alcohol	Partial	+	+
Isobutyl alcohol	−	+	+
Isopropyl alcohol	+	+	+
Isoamyl alcohol	+	+	+
Mixed amyl alcohols	Partial	+	+
Diacetone alcohol	+	+	+
Diethylene glycol	−[b]	−	+[c]
Propylene glycol	−[b]	−	+[c]
Acetone	+	+	+
Methyl acetate	+	+	+
Ethyl acetate	+	+	+
Butyl acetate	+	+	+
Amyl acetate	+	+	+
Mixed amyl acetates	+	+	+
Ethyl ether	+	+	+
Isopropyl ether	−	+	+
Dichlorethyl ether	+	+	+
Dioxan	+	+	+
Cellosolve	+	+	+
Methyl cellosolve	+	+	+
Diethyl cellosolve	+	+	+
Butyl cellosolve	+	+	+
Butyl carbitol	+	+	+
Benzene	+	+	+
Xylene	+	+	+
Toluene	+	+	+
Mixed amyl chlorides	+	+	+
Chloroform	+	+	+
Ethylene dichloride	+	+	+
Ethylene chlorhydrin	+	+	+
Chlorobenzene	+	+	+
Benzyl chloride	+	+	+
Castor oil	Ppts.	−	+
Cod liver oil	−	Partial	+
Cottonseed oil	−	Partial	+
Boiled linseed oil	−	Partial	+
Turpentine	−	+	+
Gasoline	−	Partial	+
Benzyl benzoate	+	+	+
Benzaldehyde	+	+	+

[a] + = completely soluble; − = insoluble.
[b] Swells.
[c] Emulsifies.

and Johnson (*2*). The refractive index of the fused form of the substance was $n_{\mathrm{D}}^{20} = 1.4660$.

Some electrical properties of sucrose octaäcetate are as follows:

	60 CYCLES	10^3 CYCLES	10^6 CYCLES
Dielectric const.	4.3	4.5	4.7
Power factor, %	12.3	5.8	1.7

Resistivity = 1.5 × 10^8 megohm-cm.

The amount of free acid (acetic) contained in the crystals, after washing and drying, averaged in most cases about 0.03 per cent. The stability of the compound to water, made by boiling one gram with water for one hour, showed by titration that 0.25 per cent of all available acetic acid was split off by hydrolysis. In water at 40° C. for 5 days the hydrolysis amounted to 0.20 per cent of the available acetic acid. The solubility of the compound in water was 0.14 per cent. It is intensely bitter; between 0.001 and 0.002 mg. in one cc. of water can be detected by taste. The solubility in other solvents is listed in Table I.

SUCROSE OCTAPROPIONATE AND OCTABUTYRATE

Sucrose octapropionate and the octabutyrate were prepared in a somewhat similar manner. The first, a low-melting crystalline solid, was found to form, after fusion, a semi-hard glass readily crystallizable when submerged in water, although its solubility in this solvent was less than 0.01 per cent. Its melting point was 45.4° to 45.5° C. and its viscosity measured at 48.9° C. was 47.8 poises. The density at 20° was 1.1849.

Sucrose octabutyrate, which is an uncrystallizable viscous sirup, exhibited a decidedly oily character. Its viscosity measured at 25.9° C. was 32.7 poises. The Saybolt viscosity at 210° F. (98.9° C.) was 120 seconds, and at 100° F. (37.8° C.), 2400 seconds. The density measured at 20° C. was 1.1232. Its solubility in water was similar to that of the octapropionate—i. e., less than 0.01 per cent.

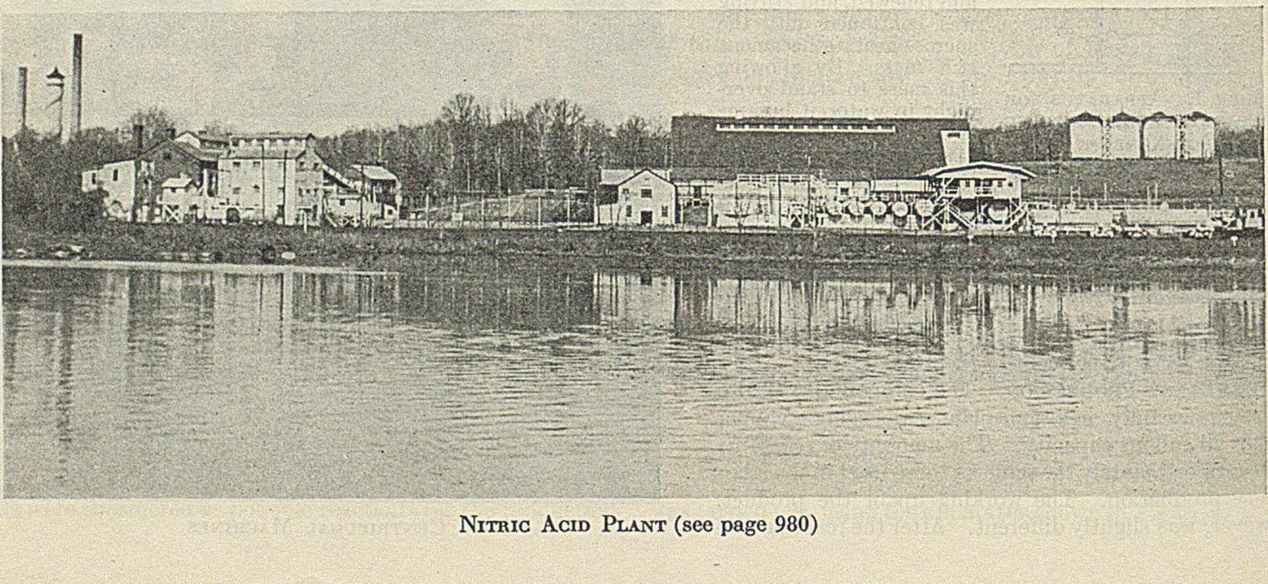
The solubilities of the esters of sucrose previously mentioned, as shown in Table I, were found by observing the behavior of 0.5 gram of solute in 5 cc. of solvent.

Further investigations on the properties and applications of these compounds are being undertaken.

LITERATURE CITED

(1) Herzfeld, A., *Z. Ver. deut. Zucker-Ind.*, 37, 422 (1887).
(2) Hudson, C. S., and Johnson, J. M., *J. Am. Chem. Soc.*, 37, 2753 (1915).
(3) Schutzenberger, P., *Compt. rend.*, 61, 485 (1865).

RECEIVED April 13, 1933.



NITRIC ACID PLANT (see page 980)

Flexible Alkyd Resins

R. H. Kienle and P. F. Schlingman, General Electric Company, Schenectady, N. Y.

The general theory of synthetic resin formation is reviewed. The development of permanently flexible alkyd resins, their preparation and properties are given. These newer alkyd resins are shown to have industrial possibilities as film-forming materials in the paint and varnish industry, and as a celluloid substitute or as an artificial rubber in the plastic industry.

PREVIOUS publications (*8*) have described three general classes of alkyd resins—namely, heat-nonconvertible, heat-convertible, oxygen-convertible. It has been shown that hard, soft, or balsam-like resins could be prepared in each class. Recently another physical property, flexibility, has been improved so that now resins are possible possessing flexibility down to a temperature of approximately 5° C. To a degree, flexible alkyd resins were available before; Callahan (*1*) obtained certain flexible effects in the heat-convertible alkyd resins by using definite dibasic aliphatic acids, and it is well known that the oxygen-convertible resins (*8*) become more flexible as the oil-glyceride content of the alkyd resins is increased. However, these flexible properties, thus induced, are only temporary, as all these modified resins when aged at the higher temperature—e. g., over 100° C.—rapidly lose their flexibility and become fairly rigid owing either to continued polymerization or oxidation. It has been possible not only to produce flexible alkyd resins but to control the degree of flexibility as well within the temperature limits specified. With this controlled flexibility a certain plasticity was observed to have been simultaneously introduced allowing compounding on rubber rolls, calendering, and pressing of the more flexible forms.

Theory of Flexible Resin Formation

In the theory of resin formation originally suggested by Kienle and Hovey (*9*) and developed in detail by Kienle (*7*), it was shown according to postulates 1 and 2, that whenever the reactivity of an organic reaction was (2,2)—that is, where the individual reacting molecules each possessed two possible points or positions of primary valence linkage—an amorphous or resinous substance resulted; unless, as Carothers (*3*) and co-workers have shown, the total number of primary valence bonded atoms between any two such successive linkages equaled five, six, or seven. In the latter case cyclic compounds are formed which result in crystalline compounds. It was further brought out in the theory of resin formation that the resins formed from reaction reactivities of (2,2) were heat-nonconvertible, owing to the fact that molecular union could give only long chains. Intertwining (i. e., crisscrossing) between molecules of high molecular weight was not possible, and therefore a gel structure did not occur. The glycol phthalates (*10*), styrenes (*15*), glycol–dibasic acid aliphatic esters (*4*), and vinyl resins (*16*) all substantiated this viewpoint. The work on rubber (*13*) and cellulose (12), both naturally occurring flexible bodies, further suggested that, if a long chain could be synthesized, flexibility, elasticity, etc., should result. Such molecules, according to the x-ray measurements, should be built up from unit molecules having a small cross section compared to their length; that is, long side chains and cyclic members should be absent. The polyesters derived from dihydric alcohols and dibasic aliphatic acids or their anhydrides satisfy these requirements; indeed Carothers (*6*) has shown that flexible, elastic fibers can be prepared from these bodies if the esterification is so carried out that a long total chain length is built up. The ordinarily prepared dihydric alcohol–dibasic aliphatic polyesters are waxes or amorphous white solids (*5*), although when molten they are distinctly transparent, heat-nonconvertible polymers.

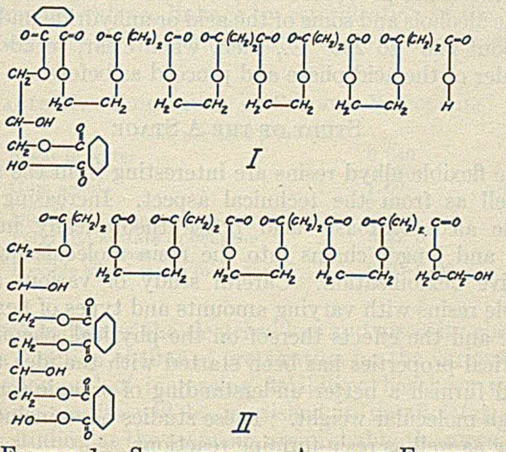


Figure 1. Structure of Average Flexible Alkyd Resin Molecule

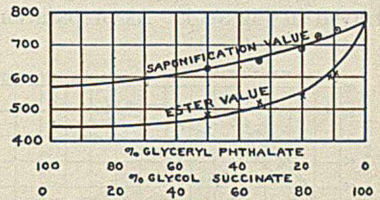


Figure 2. Variation of Saponification Value and Ester Value as Function of Mole Percentage Composition

Taking into account postulate 3 of the resin formation theory, if these long-chain molecules were attached through primary valence linkage to heat-convertible resin molecules—e. g., glyceryl phthalate—flexible heat-convertible resins should result. The mole ratio between the rigid heat-convertible phase of the resin (e. g., the glyceryl phthalate) and the long-chain, heat-nonconvertible phase (e. g., the dihydric alcohol–dibasic aliphatic ester such as glycol succinate) should determine the flexibility and plasticity; the higher the latter, the more flexible and plastic the resin. Experiments have proved these contentions (*11*). Heat-resisting, flexible alkyd resins were prepared in this manner, and, what was perhaps more important, the resins showed that a method was now available whereby the flexibility of alkyd resins could be controlled as desired.

An extended study of flexible alkyd resins has been made. Modifications have been prepared by varying the dihydric alcohol to include such glycols as diethylene glycol, triethylene glycol, tetramethylene glycol, hexamethylene glycol, etc., as well as by varying the dibasic aliphatic acid or anhydride to include such acids as adipic, sebacic, maleic, etc. Furthermore, oxygen-convertible, flexible alkyd resins have been made by introducing into the resin molecule oxidizable fatty acids, drying oils, natural resins, etc. In other words, all previously known forms of alkyd resins have been prepared in flexible form.

These studies have shown that the structure of the flexible resins are not quite as simple and straight forward as suggested above. However, the general theory is basically correct; but, in any given flexible series—i. e., with any fixed dihydric alcohol–dibasic acid flexibilizer—there seems to be a definite mole ratio of flexible to rigid resin phase beyond which, while the resulting cured resin is increasingly more flexible, the flexibilization does not continue as entirely within the molecule. Rather it increases because of the presence of the free flexible phase or low resin polymers thereof, either in solid solution in the resin or, speaking more strictly, as heavily solvating the pure resin molecules. In the case of glycol succinate, this mole ratio appears to be about 4:1; in the case of glycol adipate it is about 3:1. Whenever resins of higher mole ratio than the above are prepared, cured, and swollen in solvents, such as chloroform or dioxan, it was found that glycol succinate or glycol adipate could be precipitated from the decanted swelling agent by adding inert solvents, such as benzene or water. Such was not found to be the case with the resins of lower mole ratio. Facts such as these, augmented by analytical, solubility, physical, and electric loss data and further supported by x-ray investigations made both on the pure resins and resins treated with sundry oxides, lead to the suggestion that the average flexible alkyd resin molecule in any homologous series of flexible resins of various ratios builds up gradually to a unit cell structure as portrayed in Figure 1. As preparation of the resin proceeds, cross-tying between molecules probably takes place, brought about by the polyvalent acids or anhydrides effecting a three-dimensional molecular rigidity accompanied by the attending phenomenon of gelation. With the resins of low mole ratio the average length of the flexibilizing chains in the resin molecule is probably shorter than given in the formula. In the case of the resins of high mole ratio some flexibilizing side chains of longer length are undoubtedly formed, but the average molecules are built up from molecular structural units such as shown in Figure 1, and the entire heterogeneous molecular mixture is solvated with dihydric alcohol–dibasic acid polyester molecules.

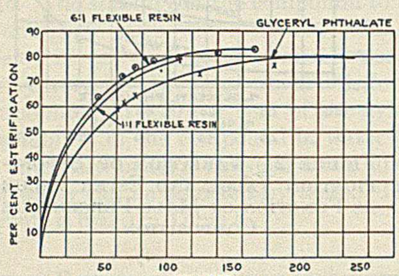


Figure 3. Variation of Percentage Esterification for Three Resins

Throughout this work a mole of glyceryl phthalate has been assumed to be glyceryl triphthalate: glycerol 184 parts by weight, phthalic anhydride 444 parts by weight. A mole of the flexibilizing ester has been assumed to be: dihydric alcohol one mole, dibasic acid one mole—e. g., glycol 62 parts by weight, succinic acid 118 parts by weight.

Preparation

One of the preferable ways to prepare this type of alkyd resin is to place all ingredients in a three-neck, round-bottom flask, heated by means of an oil bath. The flask should be equipped with a stirrer, thermometer, and short air-cooled reflux condenser. After the ingredients are molten, the stirrer is started and the temperature slowly raised to 190–200° C. The temperature is maintained at this point, water slowly escaping from the reflux until a small drop of resin on a clean 200° C. hot plate gels in 40 to 50 seconds. The reflux condenser is then removed or the resin poured into an open beaker and further heated until a 10- to 15-second cure is reached. At this point the resin may be cut with solvents, poured into shallow pans for A-stage resin, or poured into pans and placed in suitable ovens to cure for B- and C-stage resin according to the requirements. To cure, temperatures from 125° to 200° C. can be used but 150° is preferred. B-stage resin is obtained after 12 to 36 hours of curing and is that stage when the resin is just thoroughly gelled. Thoroughly cured or C-stage resin takes from 3 to 12 weeks to form in thickness of 0.25 to 0.5 inch, depending on the temperature and oven ventilation.

Typical flexible resin formulas are the following:

Mole Ratio	Mole Per Cent	Formula	Parts by weight
1:1	50	Glycerol Phthalic anhydride	184 444
	50	Glycol, ethylene Succinic acid	62 118
4:1	20	Glycerol Phthalic anhydride	184 444
	80	Glycol, ethylene Succinic acid	248 472

Other methods for preparing the resins are: open cooking with stirring, reflux throughout, reflux followed by vacuum treatment, and cooking under a current of inert gas. There are some differences observable between the various methods but, in general, the final cured resins are equivalent. The principal requirement is to keep the initial temperatures below 190° C. until the glycol has sufficient time to react thoroughly. This is necessary because of the high vapor pressure of glycol. Unless the glycol is thoroughly reacted and combined in the resins, quite different resins result.

In the preparation of flexible resins modified with drying oil acids, oils, or natural resins, the order of the addition of ingredients in some cases becomes important. Also it is generally advisable with these resins to use higher temperatures, especially when reacting the oils or oil acids. Therefore, the usual procedure is to react the oils with the polyhydric alcohols and some of the acid or anhydride under reflux at about 220° to 230° C., then, when clear, to add the remainder of the acid phase and proceed as before.

Study of the A Stage

The flexible alkyd resins are interesting from the scientific as well as from the technical aspect. Increasing the dihydric alcohol–dibasic acid phase theoretically introduces more and longer chains into the resin molecules with progressive flexibilization. Careful study of various series of flexible resins with varying amounts and types of flexibilizing phase and the effects thereof on the physical, chemical, and electrical properties has been started with the idea that this would furnish a better understanding of organic compounds of high molecular weight. These studies have included both curing as well as resin-forming reactions.

In Table I are summarized some of the properties observed in a series of increasingly flexible resins, glycol succinate being used as the flexibilizing phase. All the resins were clear, transparent, and amber colored. They varied in hardness from the 1:1 resin, which was similar to A-stage glyceryl phthalate, to the 10:1 resin which was soft and sticky like natural asphalt.

In the preparation of any series of resins, identical conditions of preparation were employed. All the resins were carried to a 10-second cure—i. e., just short of gelation.

TABLE I. PROPERTIES OF SERIES OF FLEXIBLE ALKYD RESINS (A STAGE)

(Temperature of preparation, $T = 200°$ C.)

Mole Ratio	Mole Per Cent Glyceryl phthalate	Mole Per Cent Glycol succinate	Flow Point ° C.	Acid No.	Saponification Value	Ester Value	Esterification %
..	100	0	120	123	568	445	78.5
1:1	50	50	123	133	622	489	78.5
2:1	33	67	67	144	657	513	78.2
4:1	20	80	55	153	694	541	78.0
6:1	14.3	85.7	50	141	723	582	80.5
8:1	11.2	88.8	60	134	729	595	82.0
10:1	9.1	90.9	55	129	735	606	82.5
..	0	100	...	...	...	(776)[a]	..

[a] Theoretical for neutral ester.

Table I shows that, as the mole ratio of glycol succinate increases, the flow point decreases until the 4:1 ratio is reached, whence a more or less constant value is obtained. The probable significance of this has already been discussed.

The acid number progressively increases, then decreases. The saponification value progressively increases; consequently, the ester value and percentage esterification at gelation increase. The increase in the latter, although not very appreciable, is definite. The decrease in acid number is attributed to the fact that in the high ratio resins a high percentage of heat-nonconvertible phase is present, increasing the mobility, and simultaneously the chance contact between reacting groups, thereby improving esterification.

In Figure 2 is shown graphically the variation of saponification value and ester value as a function of mole percentage composition. In both cases a regular and progressive change is observed, the difference between the two curves representing the unesterified portion of the resins.

In order to ascertain whether the mechanism of formation of the flexible resins is the same as that of the other alkyd resins, a kinetic study was made by following such factors as cure time, acid number, insulation resistance, percentage esterification as a function of time. In Figure 3 one of these variables (percentage esterification) has been plotted for three resins—namely, glyceryl phthalate, 1:1 flexible resin, and 6:1 flexible resin. Comparison with glyceryl phthalate shows that the flexible resins are built up in a uniform continuous manner analogous to the other alkyd resins, except at different rates depending upon composition. In other words, primary valence linkage by esterification of the interacting molecules is the fundamental resin-forming reaction.

TABLE II. COMPARISON OF SPECIFIC VISCOSITIES

(One per cent solutions)

Sugar in water	0.040
Latex	0.025
Gum arabic	1.00
Starch	0.05
Nitrocellulose in ethyl lactate	2.00
Polyvinyl acetate in benzene	5–22.5
Rubber in benzene	7.5–12.5
Flexible alkyd resins in dioxan	0.03–0.09

An investigation of the electrical loss and viscosity changes, both as a function of time of preparation for the various individual resins and of increasing flexibility, has been carried out. These results will be published in detail later. The viscosity studies, at the moment, are probably the more interesting in view of the recent work of Staudinger (*14*) in using viscosity as a tool in investigations of high molecular weight organic compounds. Dry distilled dioxan was used as the solvent in these viscosity studies because of its nonpolar character and its good solvency for all ratios of resins.

The viscosity investigations revealed that in all cases it was possible to work with solutions up to 10 per cent weight concentrations. The viscosities of the dioxan solutions were lower than anticipated, either because of the good solvent power of dioxan or because the actual molecular size of the resin molecules, at least in dioxan solution, is smaller than the solid state would suggest; i. e., they are on the average either as given in Figure 1 or very small multiples thereof. This is best illustrated by the specific viscosity values of one per cent dioxan solutions which varied between 0.03 and 0.09 for all the resins measured. In Table II a comparison of the specific viscosities of other colloids in one per cent solutions of suitable solvents is given.

A regular family of viscosity–time of preparation curves was obtained for a given resin series shifting on the time axis with the composition. In all the cases, as the reaction proceeded, there was but a slight change in viscosity noted until gelation was approached, after which a very rapid rise occurred. By plotting specific viscosity against percentage esterification, the value of the specific viscosity at a common percentage esterification near the gel point for all resins—namely, 80 per cent—was obtained from the curves. These values are given in Table III and are plotted against percentage mole composition in Figure 4. The specific viscosity falls steadily as the percentage flexible phase increases to about 65 per cent, then holds steady to about 80 per cent, followed by another downward trend. The importance of the 4:1 ratio is again demonstrated.

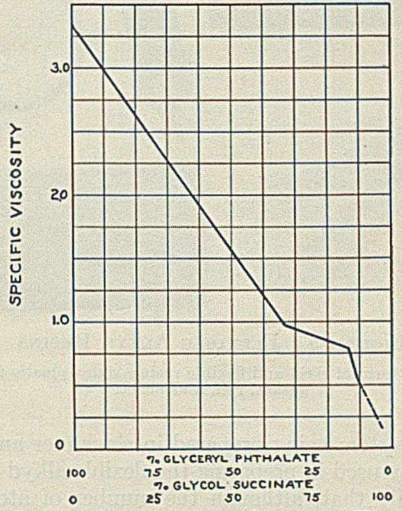


FIGURE 4. PLOT OF SPECIFIC VISCOSITY *vs.* PERCENTAGE MOLE COMPOSITION

TABLE III. SPECIFIC VISCOSITIES AT 80 PER CENT ESTERIFICATION

Mole Ratio	Mole Composition Glycol succinate	Mole Composition Glyceryl phthalate	η_{sp} at 80%
0:1	0	100	3.34
1:1	50	50	1.55
2:1	66.7	33.3	0.96
4:1	80.0	20.0	0.88
6:1	85.7	14.3	0.80
8:1	88.8	11.2	0.56

A study was made of the effect of the composition of the flexible phase on flexibility. Other glycols, such as diethylene, decamethylene, hexamethylene, etc., were substituted for ethylene glycol and all the straight-chain dibasic aliphatic acids up to and including sebacic acid were studied. The effect of increasing the length of either the dihydric alcohol or the dibasic acid molecule was to increase the flexibility for any mole ratio. Thus a 2:1 cured glycol adipate resin was found to be approximately equivalent to a 3:1 cured glycol succinate resin. However, the increased flexibility was less than anticipated from similar studies with glyceryl phthalate. On the assumption that the length of the introduced chain determined the flexibility, it is readily seen that the vital factor is not the length of the structural unit, but the average length of the actual polyester chain that these structural units build—in other words, the actual number of atoms per average polymolecule. In the last column of Table IV this value is given for a number of polyesters. The values were obtained from data published by Carothers and co-workers (*2*), the polyesters being prepared in a manner analogous to that normally used in preparing the flexible alkyd resins. It is seen readily that, although the number of atoms in the structural units varies considerably, the average number of structural units compensates for this fact so that the total number of atoms per average polymolecule actually varies but little. This is in agreement with the flexibility as observed with the various substituted flexible resins. Values for cellulose and rubber were included in Table IV, showing that a value of about 600 atoms per average polymolecule, or better, is necessary to give real fiber structure, a hypothesis which Carothers' superpolyesters supports.

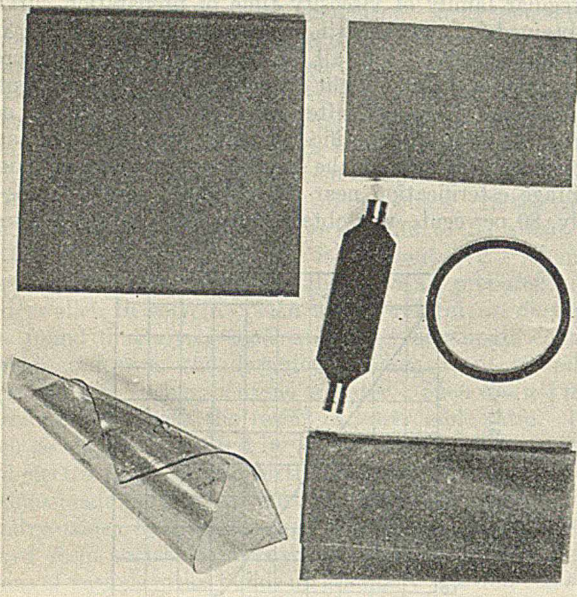


FIGURE 5. FLEXIBLE ALKYD RESINS

Left, cast form of rigid and flexible resin; right, plastic form as gasket, roll, and sheet.

TABLE IV. TOTAL ATOMS IN POLYMOLECULE CHAIN

COMPOUND	*A* Atoms in chain of structural unit	*N* Av. structural units per mol.	($A \times N$) Total atoms per av. polymol.
Ethylene succinate	8	20	160
Hexamethylene succinate	12	14	168
Ethylene adipate	10	17	170
Decamethylene adipate	18	10	180
Ethylene sebacate	14	13	182
Cellulose	10	60–100	600–1000
Rubber	4	10,000	40,000

THE B AND C STAGES

The gelled and cured stages of the flexible alkyd resins are marked by the progressively increasing flexibility and plasticity of the resins as the mole ratio of di-di polyester is increased. This is illustrated in Table V, which also gives hardness and elasticity data as measured by the Shore hardness gage and elastometer, respectively, for both the cured and plastic forms. The permanency of these cured flexible resins to aging has already been described. Further differentiation from the earlier modified resins is obtained by comparing a cured 2:1 glycol succinate resin with a cured glycerol succinic acid–phthalic anhydride resin, formulated to the same acid ratio, with regard to the action of certain solvents. When cured pieces of both were submerged in chloroform, the former gradually imbibed solvent and swelled, while the latter was practically unaffected. Similarly, when cured pieces of both were placed in a bottle containing equal volumes of chloroform and 25 per cent caustic soda solution, the former sank into the chloroform layer, swelled, and remained there while the latter floated on the chloroform in the caustic soda layer, gradually disappearing as saponified. Both of these tests show a marked difference between the two resins, the action of the chloroform being explained by the fact that it is a solvent for glycol succinate and hence wets the resin containing glycol succinate polyester chains.

TABLE V. COMPARISON OF CERTAIN PHYSICAL PROPERTIES OF A CURED, FLEXIBLE RESIN SERIES

RESIN MOLE RATIO (Glycol succinate)	CAST SHEETS		PLASTIC SHEETS		REMARKS
	Shore hardness	Shore elasticity	Shore hardness	Shore elasticity	
1:1	99	..	100	..	Very tough, stiff, hard
2:1	97	..	100	..	Tough, hard, bendable
4:1	95	33	100	..	Tough, flexible
6:1	83	38	74	43	Tough, very flexible
8:1	63	95	49	88	Rubbery, exceedingly flexible
10:1	55	95	39	95	Very rubbery

The flexible resins can be cast into sheets or rods and cured. In the cured state the harder resins of any given series are particularly interesting as they are exceedingly tough, yet pliable. Colored, transparent, and pigmented effects can be obtained. The cured resins can be milled, machined, polished, and even formed by heat and pressure into simple shapes. They offer a substitute for celluloid with the added advantage of noninflammability.

Cured sheets of the very flexible resins possess the property of sound absorbency and vibration dampening. The latter property may be observed by dropping a coin on a sheet, say, of cured 8:1 resin. The coin simply lands with a thud and rests without further movement.

The cured flexible resins, because of a certain plasticity induced by the flexibilization, can be compounded on rubber rolls and handled very much like rubber (*17*). By adding fillers and a binding resin, plastic alkyd resin compounds of various degrees of plasticity and flexibility can be prepared. Such compounds can be sheeted, calendered, and cured. They test and act, except in magnitude of stretch and method of curing, like ordinary rubber compounds. To cure, temperatures over 125° C. are used, the curing time varying from 2 to 100 hours, depending on the size of piece and the temperature. Dry heat is always used. Under no condition should a steam autoclave be employed, as high-pressure steam tends to hydrolyze the resin. The usual practice is to wrap the article with cloth or gauze and cure in an open oven; the cloth or gauze, being porous, allows the escape of volatile matter vital to the curing. Owing especially to the heat resistance and oil-proof characteristics of the alkyd resins, these newer plastic forms are finding use as gaskets, and as oil- and gasoline-resistant materials.

The flexible alkyd resins, both straight and modified, are finding use in the paint and varnish industry wherever flexibility is a paramount requirement. They are being employed as plasticizer resins in lacquers and as the base for certain improved heat- and oil-resisting varnish cloth. Undoubtedly their use will extend with time.

It is of particular interest that these flexible resins, being simply polyesters and not polydienes like natural and synthetic rubbers, are so rubber-like in character. This physical similarity and chemical difference, in view of what is known of their structure, seems to be additional proof of the fundamental chain structure of the natural rubber molecule.

In conclusion, it is evident that we now have available alkyd resins with definite and controlled flexibility. This has been accomplished in a new manner, not by adding external plasticizers and flexing agents, but actually by introducing these properties into the resin molecule through intentional formulation.

Literature Cited

(1) Callahan, M. J., U. S. Patent 1,091,732 (Mar. 31, 1914).
(2) Carothers, W. H., *Chem. Rev.*, 8, 353–426 (1931).
(3) Carothers, W. H., *J. Am. Chem. Soc.*, 51, 509 (1929).
(4) Carothers, W. H., and Awin, J. A., *Ibid.*, 51, 2560 (1929).
(5) Carothers, W. H., and Dorough, G. L., *Ibid.*, 52, 711 (1930).
(6) Carothers, W. H., and Hill, J. W., *Ibid.*, 54, 1579 (1932).
(7) Kienle, R. H., Ind. Eng. Chem., 22, 590 (1930).
(8) Kienle, R. H., and Ferguson, C. S., *Ibid.*, 21, 349 (1929).
(9) Kienle, R. H., and Hovey, A. G., *J. Am. Chem. Soc.*, 51, 509 (1929).
(10) *Ibid.*, 52, 3636 (1930).
(11) Kienle, R. H., and Rohlfs, H. C., U. S. Patent 1,897,260 (Feb. 14, 1933).
(12) Meyer, K. H., and Mark, H., *Ber.*, 61, 593 (1928).
(13) Pickles, S. S., *J. Chem. Soc.*, 98, 1085 (1910).
(14) Staudinger, H., "Die hochmolekularen organischen Verbindungen," Springer, 1932.
(15) Staudinger, H., Brunner, M., Frey, K., Garbsch, P., Signer, R., and Wehrli, S., *Ber.*, 62, 241 (1929).
(16) Whitby, G. S., McNalley, J. S., and Gallay, W., *Trans. Roy. Soc. Canada*, 22, 27 (1928).
(17) Wright, J. G. E., *Chem. & Met. Eng.*, 39, 438 (1932).

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Pressure-Temperature and Low Pressure Total Heat Relationships of Petroleum Fractions

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A method of identifying the equivalent pure cut of a wide-cut fraction has been developed, and data have been analyzed to show that the critical point for such a cut constitutes the common point of convergence for the dew lines of all similar wide-cut fractions of equal gravity. This equivalent pure-cut critical point can also be used as a guide for the development of wide-cut boiling lines and partial vaporization effects. Finally, the equivalent pure cut can be used as a basis for calculating the total heats of low-pressure petroleum fraction vapors.

In an effort to develop a method for predicting the dew and boiling lines for petroleum fractions, vapor pressure charts have been devised by various investigators from the data of the pure compounds, particularly the pure paraffins. The common aim of these investigators has been to produce a chart on which the vapor pressures of the pure compounds plot as straight lines converging at a single point. The coördinate system described by Maxwell (*5*) accomplishes this purpose remarkably well; hence it has been used in the following discussion.

While a family of radiating straight lines drawn on such a chart as Maxwell's represents the pure compound data within engineering accuracy, large errors may occur when these pure-cut lines are used for estimating the dew and boiling lines for petroleum mixtures, since the lines for such mixtures cut across the pure-compound lines at various angles, depending on the width of the cut (i. e., its boiling range). Consequently, some method of evaluating the changes of slope of the wide-cut lines must be developed before a vapor pressure chart for a pure compound can be accurately applied to wide-cut petroleum fractions.

A method of attacking this problem was suggested by Bahlke and Kay's study (*2*) of the thermal properties of two petroleum distillates which differed only in boiling range. The heavy loops on Figure 1 are plots of Bahlke and Kay's vapor pressure data for these two distillates. The upper, dashed line of each loop is the dew line—that is, the line of complete vaporization or initial condensation for the cut in question—while the lower, solid line is its vapor pressure line, or line of initial vaporization, or complete condensation. At any given pressure, the indicated temperature gap between the dew line and the boiling point line is the boiling range of the distillate for that particular pressure, and points between the dew and boiling lines indicate various conditions of partial vaporization. The difference in the spread of these two loops is brought about entirely by the difference in boiling range, since the two cuts were of the same A. P. I. gravity and molecular weight, and hence, for thermal purposes, of the same composition.

Equivalent Pure Cuts

When the observed boiling and dew points of the two Bahlke and Kay fractions were plotted against boiling range for several different pressures, as in Figure 2, and straight lines drawn through the respective points, the straight lines were found to intersect on the ordinate for zero boiling range, thus defining a series of boiling points for a hypothetical hydrocarbon of zero boiling range. Furthermore, when these hypothetical boiling points were, in turn, plotted on the vapor pressure chart of Figure 1, they were found to fall exactly along a pure-compound line; that is, they fell on a straight line which, when extended beyond the range of the chart, passed through the common point of convergence for all other pure-hydrocarbon vapor pressure lines. But the hypothetical pure cut represented by such a line would have the same gravity and molecular weight as the two actual cuts from which it was derived; consequently, this zero boiling range cut could be considered as the equivalent pure cut of the actual wide-cut fractions. Such an equivalent pure cut furnishes a basis for the measurement of the effect of boiling range on the slope of the dew and boiling point curves of a wide-cut fraction, since all wide-cut fractions of the same gravity and molecular weight can be considered

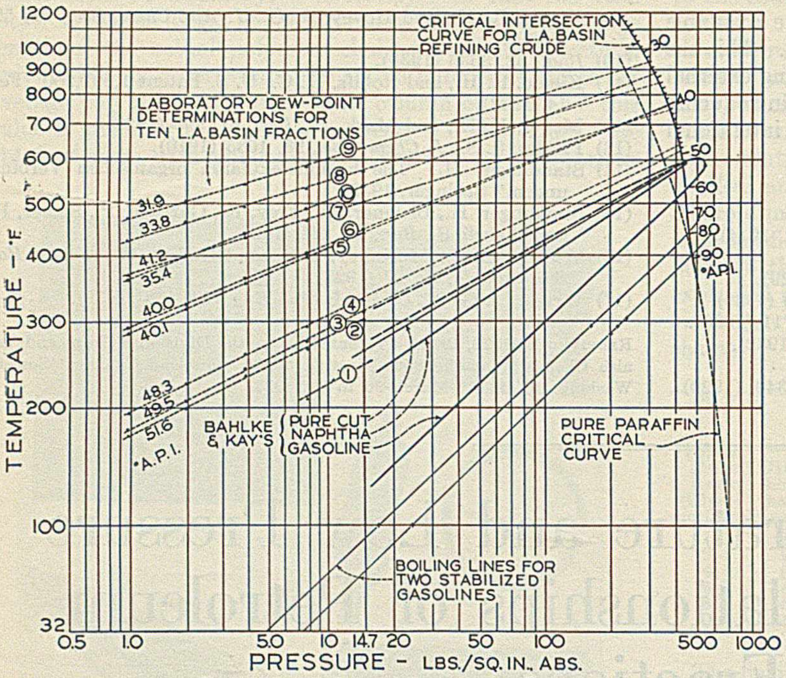

Figure 1. Vapor Pressure Chart

as having been derived from a single equivalent pure cut by the spreading out of their dew and boiling lines through fractional blending.

Critical Intersections

In order to make use of this conception of a hypothetical pure cut, it was necessary to find some property common to this cut and to all the wide cuts derived from it, which would not be affected by boiling range. Three cuts as closely related as Bahlke and Kay's two actual cuts and their equivalent pure cut could well be expected to have at least one point in common in the pressure-temperature plane. The dew lines of the two Bahlke and Kay cuts almost intersect at one point on Figure 1 (595° F. and 435 pounds per square inch absolute); and in confirmation of the above supposition, the point of closest approach of these two dew lines was found to lie close to the critical point of the equivalent pure cut (located by methods described later). This led to the hypothesis that, within engineering accuracy, the critical point of an equivalent pure cut can be taken as common to the dew lines of all corresponding fractions of equal gravity, regardless of width of cut. For brevity, such points have been called "critical intersections."

The value of this concept of a critical intersection lies in the fact that it extends the range of usefulness of the vapor pressure chart to include the wide-cut type of fraction normally encountered in petroleum refining practice. The above described critical intersection points appear to bear the same relation to the dew lines of wide-cut fractions that the common point of convergence bears to the dew lines of pure compounds; although a different set of critical intersection points will be required for the cuts from each given crude source, whereas the common convergent for the pure compounds remains fixed for all classes of hydrocarbons.

Location of Critical Intersections by the Aid of Laboratory Data

The critical intersection point for a fraction cut from any given type of crude can be identified by gravity alone. Such an identification, however, requires a preliminary laboratory determination of the gravity–dew point relationships of a series of fractions cut from the crude in question.

The required dew point data may be readily determined in the laboratory by the aid of the continuous dew point still shown in Figures 3 and 4. This still has been reduced to a piece of routine laboratory apparatus by means of which dew points can be easily obtained by the ordinary operator. By suitably controlling its heating and rate of feed, the amount of liquid retained in such a still can be held constant, and the overhead distillation rate maintained equal to the feed rate. Hence, as distillation proceeds, the composition of the retained liquid will change until it reaches equilibrium with the vaporized feed material. After this equilibrium has been attained, the composition of the incoming feed and outgoing vapors will be the same, and the vapor outlet thermometer will record the dew point of the feed material at the still pressure.

This dew point still is readily operable at absolute pressures down to 100 mm. For critical intersection calculations, laboratory dew points should be obtained on the desired wide-cut fractions for a series of pressures ranging from 100 to 760 mm.

After obtaining the necessary laboratory dew point data, the critical intersection and equivalent pure-cut values for the wide-cut fraction can be graphically determined as indicated on Figure 5, where the method has been applied to a Los Angeles Basin cut.

For this graphical solution, the laboratory dew point data are plotted on a Maxwell vapor pressure chart, and a straight line is drawn through these points and extrapolated out into the critical region. It has already been noted that the critical intersection for a wide-cut fraction is practically identical with the critical point of an equivalent pure cut which has the same gravity as the wide-cut fraction. Consequently, the solution of the critical intersection problem involves the identification of a hypothetical pure cut having a gravity equal to the wide-cut gravity, and a vapor pressure curve which intersects the wide-cut dew point line at the critical temperature of the pure cut.

Eaton and Porter (3) have recently published a relationship between gravity, atmospheric boiling point, and critical temperature for pure hydrocarbons. This relationship (which is expressed by the curve of Figure 6 with the exception that the extrapolated high-temperature section has been drawn in somewhat higher than indicated by Eaton and Porter) can be used for identifying the desired pure-cut curve.

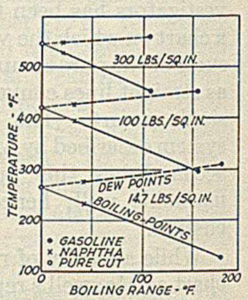

Figure 2. Extrapolation of Dew and Boiling Points of Bahlke and Kay's Fractions to Zero Boiling Range

In applying Eaton and Porter's data, two pure-cut dew lines (i. e., straight lines passing through the pure compound convergent of Figure 1) are drawn in such positions that one passes somewhat above, and the other somewhat below, the extrapolated wide-cut dew line in the critical region. Critical temperatures are then calculated for these two assumed cuts, using the atmospheric dew points indicated by the respective pure-cut intersections with the atmospheric pressure ordinate, together with the observed gravity of the wide-cut fraction, for entering the critical temperature plot of Figure 6. These calculations will give the critical points *A-A* of Figure 5. But the critical point for the true equivalent pure cut must fall exactly on the extrapolated wide-cut dew line; hence, if the two assumed pure-cut curves have been drawn fairly close to the wide-cut dew line, a straight line drawn between points *A-A* will cross the wide-cut dew line at the desired critical intersection, and a pure-cut line drawn through this point will define the equivalent pure cut of the wide-cut fraction.

CRITICAL INTERSECTION CURVE FOR A LOS ANGELES BASIN CRUDE

The critical intersection curve of Figure 1 was defined by analyzing ten Los Angeles Basin refining crude fractions as outlined above. After the critical intersection points for these ten cuts had been located, a smooth curve was drawn through them and divided into even degrees A. P. I., the gravities of the ten cuts furnishing a guide for this operation.

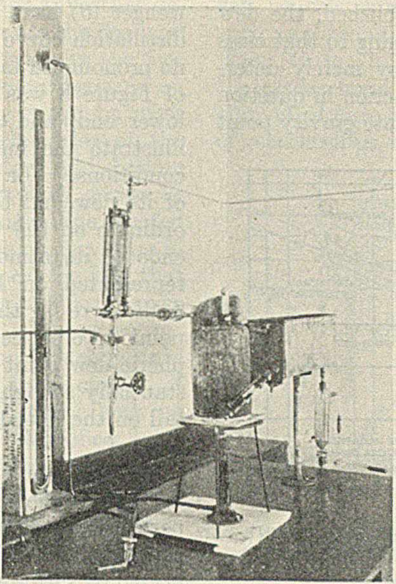

FIGURE 3. DEW POINT STILL

While the whole conception of the critical intersection relationship is based essentially on a single pair of distillates (Bahlke and Kay's), nevertheless, the consistency of the results obtained for the ten Los Angeles Basin cuts indicates that the relationship is dependable. Of the ten cuts analyzed, eight fit the critical intersection gravity scale within the drafting accuracy of the chart. Cuts 5, 6, and 7 lend particular support to the critical intersection analysis. The slopes of the dew lines, the position of the atmospheric dew points, and the gravities of these three cuts defied correlation until the critical intersection method was developed. Yet all these cuts fit exactly into the critical intersection curve.

Two of the Los Angeles Basin cuts (8 and 10) do not fit the curve as well as could be desired, their A. P. I. gravities being apparently reversed. The dew point data on which these curves are based were determined some time before the concept of a critical intersection had been advanced; consequently, it was impossible to check the reported gravities. However, there is reason to believe that the reported gravities for these two cuts were in error.

CRITICAL INTERSECTION, GRAVITY, MOLECULAR WEIGHT RELATIONSHIPS

As it has been presented, the critical intersection curve of Figure 1 is restricted to straight-run fractions from Los Angeles Basin crudes. Consequently it cannot be applied to fractions which are dissimilar from those from which it was developed. Obviously, by subjecting other types of materials to the same sort of analysis that was applied to the Los Angeles fractions, similar critical intersection curves could be developed for the materials in question. However, it appears probable that a dew point chart such as Figure 1 can be made generally applicable to all types of fractions, not by developing separate critical intersection curves for various types of materials, but by substituting for all such curves a network of gravity–molecular weight coördinates in the critical region. If this were possible, the resultant chart would become universally applicable to all types of hydrocarbons, the critical intersection point for any given fraction being then located from the gravity and molecular weight of the fraction alone, without reference to its source or composition. An attempt to develop such a gravity–molecular weight coördinate system has not been entirely successful; however, the relationships so far developed are sufficiently suggestive to warrant their inclusion in this discussion.

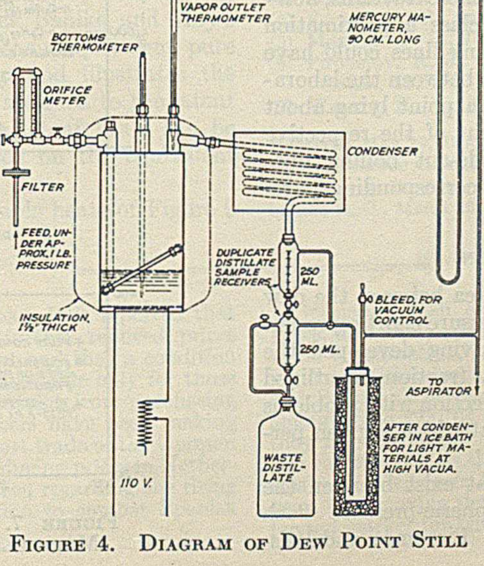

FIGURE 4. DIAGRAM OF DEW POINT STILL

Figure 7 is an enlargement of the critical region of Figure 1. All available critical data for both pure compounds and equivalent pure cuts for petroleum fractions have been plotted on this chart; the equivalent pure-cut data noted on Figure 7 include the twelve fractions previously discussed, together with eleven additional cuts not used in that development.

It is to be expected that a gravity–molecular weight coördinate system such as is plotted on Figure 7 would be warped and distorted. Nevertheless, in spite of the expected warping, lines of constant A. P. I. gravity can be readily drawn among the plotted points of Figure 7 with little distortion. While some of the points do not fall exactly where they should with respect to the gravity curves, no point will be found to be more than about 5° A. P. I. in error. It thus appears that, with a little greater precision in the graphical analysis method, a set of gravity–critical intersection curves could be drawn on the vapor pressure chart which would fall well within the desired limits of engineering accuracy.

The molecular weight curves, on the other hand, are not as consistent as the gravity curves. Many of the points are out of position with respect to the indicated molecular weight lines, some being badly in error. This last group includes Bahlke and Kay's fractions, which must be given considerable weight in discussing any such general analysis. However, consistent difficulty has been experienced in obtaining reproducible molecular weights for many of the materials indicated on Figure 7, and it is just as possible that the noted molecular weights are in error as that the points are out of position. Furthermore, extreme precision is not necessary for ordinary engineering calculations. Therefore, if a set of gravity–molecular weight coördinates can be established that generally represent the critical intersection data with reasonable accuracy, the purpose of the chart will have been fully served. Figure 7, therefore, should be viewed principally as a suggestion to other investigators regarding a fruitful field for further correlative work.

VAPOR PRESSURE LINES

After the basic critical intersection curve for a particular class of petroleum fractions has been established, the dew line for any desired wide-cut fraction belonging to that class of material can be accurately estimated by merely determining one additional dew point for the fraction in question and connecting this point with the appropriate gravity point on the critical intersection curve. The vapor pressure line (or boiling line) for such a fraction, however, cannot be so readily and surely located.

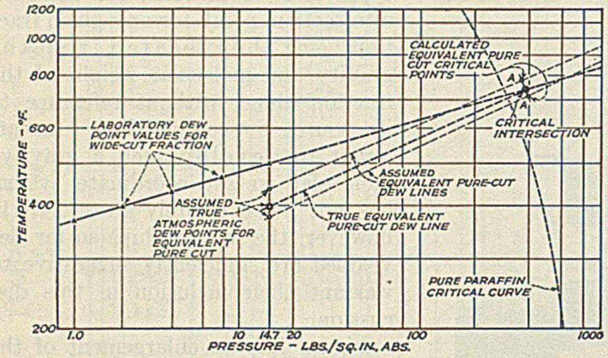

FIGURE 5. GRAPHICAL DETERMINATION OF EQUIVALENT PURE-CUT DEW LINE FOR LOS ANGELES BASIN CUT 7

At the present time, the only method available for accurately locating a vapor pressure line involves the use of two widely separated vapor pressure determinations. Although laboratory determinations are normally limited to relatively low pressures and temperatures, any pressure-temperature condition at which the material in question has existed as a liquid in equilibrium with its vapor constitutes another point on the vapor pressure line. The two stabilized gasoline boiling lines on Figure 1 were developed by such data taken from a high-pressure stabilizer. The upper points on these lines are the pressure-temperature controls carried on the stabilizer bottoms, while the 100° F. points represent laboratory vapor pressure determinations. Straight lines drawn through these points and extended to approximately the critical intersection pressure ordinate thus established the vapor pressure lines for these particular fractions. If the high-pressure points had not been available for these fractions, however, a first class approximation of their boiling lines could have been made by drawing a straight line between the laboratory determined low-pressure point and a point lying about 100 pounds per square inch to the right of the respective critical intersection points. These wide-cut boiling lines have slopes markedly steeper than the corresponding pure-cut boiling lines.

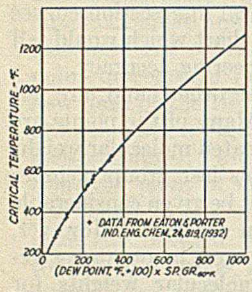

FIGURE 6. CRITICAL TEMPERATURES OF PURE HYDROCARBONS

PARTIAL VAPORIZATION

As mentioned earlier, points in the area between the dew line and the boiling line on the vapor pressure chart represent conditions of partial vaporization. Having developed the dew and boiling curves for any particular fraction as outlined above, this fact can be employed in connection with problems involving the pressure or temperature at which a given percentage of material will be vaporized.

Figure 8 shows the relationships that exist between the Engler distillation curve, an atmospheric-pressure flash curve, and a high-pressure flash curve. Piroomov and Beiswenger (*6*) have shown that the major portion of the flash distillation curve is a substantially straight line if there are no pronounced tails on the Engler curve. The Engler curve of Figure 8 was purposely drawn with a long tail on the lower end, and a normal curvature at the upper end to illustrate the methods involved in interpreting these two conditions. For any particular fraction the intersections of its dew and boiling lines with the atmospheric pressure ordinate on the vapor pressure chart definitely fix the two ends of its atmospheric pressure flash curve, such as are represented on Figure 8. Therefore, in constructing the flash curve for the subject example, the atmospheric boiling point (at 0 per cent off) should be connected with the atmospheric dew point (at 100 per cent off) by a line that is substantially straight except at the lower end, where the long tail on the initial section of the Engler curve is to be taken care of.

The curvature of the flash curve is in the same direction as that of the Engler; and while for the present only experience can dictate the amount of this curvature, we know it must be small if the dew and boiling points are to be connected by substantially straight lines. The normal curvature on the upper end of the Engler on Figure 8 would suggest that the straight middle section of the flash curve could be continued to the dew point without curvature. At the lower end, however, a slight curvature was introduced into the flash curve to correlate with the long tail on this part of the Engler.

A flash curve thus established can be used for determining the temperature at which a given percentage of material will be vaporized during continuous flash distillation at atmospheric pressure; or conversely, the percentage that will be vaporized at a given temperature.

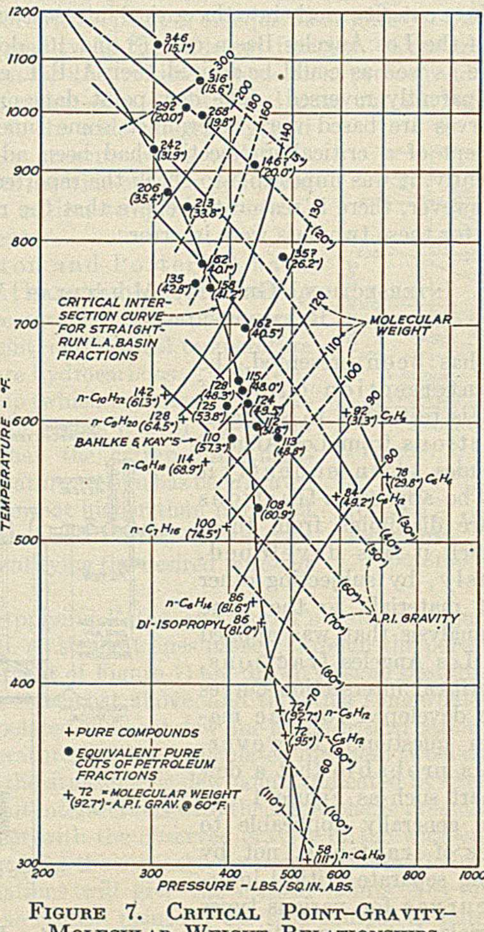

FIGURE 7. CRITICAL POINT–GRAVITY–MOLECULAR WEIGHT RELATIONSHIPS

A similar flash curve can be established for any other desired pressure in exactly the same manner, since the dew and boiling line intersections at the given pressure fix the two ends of the flash curve. The effect of increased pressure on the curvature of the flash curve of Figure 8 can be most easily visualized by considering the extreme case of the critical pressure. At this pressure the dew and boiling points are identical. The corresponding flash curve is therefore represented by a horizontal, straight line located at the critical temperature; and there can be no curvature in this line. As a generalization, therefore, it can be said that an increase in pressure tends to straighten the flash curve and make it more nearly horizontal.

Because the Piroomov-Beiswenger method has come into general use for predicting high-pressure flash curves, it might be well to point out an essential difference between their extrapolation method and the one described here. When the atmospheric-pressure flash curve is extrapolated to higher pressures by the Piroomov-Beiswenger parallel shift method, only the central portion is shifted—for example, that part from about 15 to 85 per cent off. Then some freedom is allowed in the matter of sketching tails on to the two ends of the partial flash curve thus established. In the authors' method, however, this procedure is exactly reversed, the two ends of the flash curve being first definitely fixed, and the balance of the curve then drawn in to fit these points.

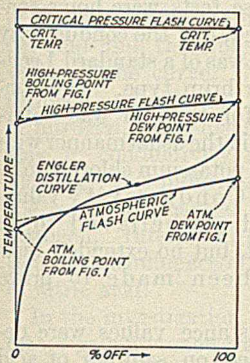

Figure 8. Equilibrium Flash Curves

Low-Pressure Total Heat Curves

At low pressures (i. e., atmospheric or lower) it is generally conceded that wide- and narrow-cut vapors alike act substantially as perfect gases. This leads to a correlative hypothesis—namely, once vaporized, wide- and narrow-cut fractions of the same molecular weight and gravity have the same total heat at any given temperature when referred to the liquid state at a common base temperature. Granting this relationship, it is possible to construct a low-pressure total heat chart for all wide-cut fractions of a given gravity and molecular weight by making use of the latent heat of their common equivalent pure cut.

Figure 9 is a typical total heat diagram on which has been shown the vaporization of three complementary cuts of given gravity and molecular weight, such as Bahlke and Kay's wide- and narrow-cut distillates and their equivalent pure cut. The diagram is self-explanatory and illustrates the fact that, whatever definition may be assigned to the latent heat of a petroleum fraction, all such latent heats can be accommodated by a single chart based on the equivalent pure cut.

The indicated liquid and vapor sensible heats of Figure 9 can be calculated by appropriate specific heat equations, such as those of Fortsch and Whitman (*4*) and Bahlke and Kay (*1*) for liquids and vapors, respectively. Similarly, the atmospheric latent heat of the pure hydrocarbon (the equivalent pure cut) can be calculated by means of a number of relationships, of which Kistyakowski's (*7*) seems to be the most reliable for large temperature extrapolations. This particular equation involves only molecular weight and atmospheric boiling point. In applying it to the construction of the total heat diagram for a petroleum fraction, the molecular weight used must be that of the fraction; and the atmospheric boiling point, that of the equivalent pure cut. The latent heat thus calculated is then added to the total heat of the liquid at the pure-cut boiling temperature, and a vapor sensible heat line passed through the dew point thus established. The low-pressure total heat of any wide-cut vapor of the same gravity and molecular weight can then be directly read off the vapor line of the resultant chart.

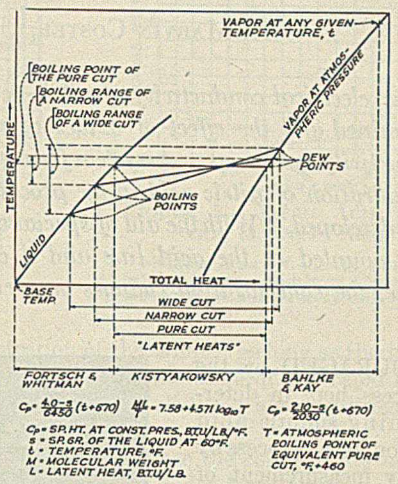

Figure 9. Total Heat Diagram

Acknowledgment

The authors wish to acknowledge the aid rendered by E. A. Wilson, G. A. Wood, and Robert Diehl in perfecting the detailed design and the technic of operating the continuous dew point still.

Literature Cited

(1) Bahlke, W. H., and Kay, W. B., Ind. Eng. Chem., **21**, 942 (1929).
(2) *Ibid.*, **24**, 291 (1932).
(3) Eaton, G. L., and Porter, C. A., *Ibid.*, **24**, 819 (1932).
(4) Fortsch, A. R., and Whitman, W. G., *Ibid.*, **18**, 795 (1926).
(5) Maxwell, J. B., *Ibid.*, **24**, 502 (1932).
(6) Piroomov, R. S., and Beiswenger, G. A., *Am. Petroleum Inst. Bull.*, **10**, No. 2, Sect. II, 52–68 (1929).
(7) Watson, K. M., Ind. Eng. Chem., **23**, 360 (1931).

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Potash Competition in Netherlands. It is reported that the Franco-German potash cartel has further reduced prices in the Netherlands market by 15 per cent and that a condition of the latest reduction is that it will be available only for those purchasing dealers, associations, etc., refraining from purchasing Spanish potash. Spanish potash producers have been making increasing inroads into the important export trade of the German industry, and the action of the latter in reducing prices in Netherlands is in keeping with its growing concern regarding the rising Spanish competition and its determination to combat Spanish imports as effectively as possible.

German potash exports have contracted heavily in recent years, and while part of the decrease has been due to curtailed world consumption, a share of the losses is attributed to increasing competition from foreign sources, notably the United States and Spain. Whereas total German exports of potash salts amounted to 222,704 metric tons in the first 5 months of 1931, they fell to 184,800 tons in the corresponding period of 1932, and to 136,847 tons this year. Shipments to Netherlands during this period fell from 86,000 tons in 1931 to only 4190 tons this year, thus moving the Netherlands from third to tenth place as a foreign market for German salts.

Application of Conductivity Measurement of Nitric Acid Concentration to Plant Control

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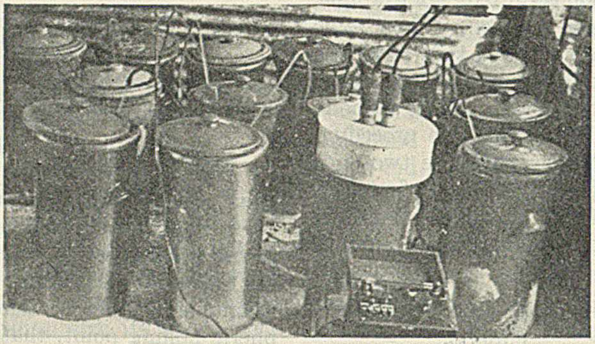
The electrical conductivity of nitric acid has been determined and the effect of oxides of nitrogen on conductivity measured. A system for measuring the concentration of nitric acid in the process itself has been developed. With the aid of special conductivity cells mounted in the acid line and a conductivity bridge, the concentration changes occurring through the whole cycle of operation can be followed, step by step, by an occasional press of an electric button. The conductivity curves and the system have resulted from the conductivity measurements and analysis of about five hundred samples, in the process, drawn from the process, and prepared in the laboratory.

Encouraged by the success here in determining sulfuric acid concentration in the process by conductivity measurement of its solutions and by the excellent results obtained on applying these measurements to plant control (*2*), attention was directed to a similar development and application to nitric acid operation.



Cells Mounted in 8-Gallon Crock of Acid to Determine the Effect of Oxides of Nitrogen on the Conductivity of Nitric Acid

Old Method

In the process for the manufacture of smokeless powder only about three-quarters of the nitric acid distilled (Figure 1) from a charge of sodium nitrate is sufficiently strong to be made into fortifying acid for use in building up or fortifying the spent acid after the nitration of cotton. The rest must first be concentrated by distillation before it too can be used. In order to effect a separation of the strong and weak, a cut is made during the run which diverts the weak fraction into a different tank from that receiving the strong. Obviously, it is important that this cut be made at such a time as will secure the maximum yield of strong acid. The old practice was to cut at so many minutes after prime (the time at which large volumes of acid vapors are rapidly delivered to the condensers) but this proved very unsatisfactory as acid strength by this method varied more than 5 per cent from day to day, resulting in a loss of strong acid and, therefore, a gain in weak which had to be redistilled at an added and unnecessary expense.

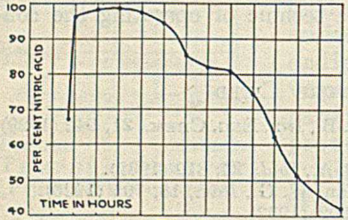


Figure 1. Nitric Acid Concentration *vs.* Time in Distillation Cycle

Development of Conductivity Method

The reciprocal of the measured resistance is the conductance of the solution. The values for nitric acid shown in Figure 2 were taken from the literature (*3*); those shown in Figures 3 and 4 were determined on chemically pure acid, prepared free of oxides and up to a concentration of 99.92 per cent in this laboratory. The cells used in these tests were home constructed, but the conductivity bridge was of a standard Leeds & Northrup type. The constant for the cell was determined in the usual manner with 0.02 *N* potassium chloride solution. Conductivity values plotted are believed to be correct, but no extended tests have been made to prove them.

Resistance values were determined on samples of acid drawn from the process. These samples covered the range of strength produced through the cycle of operation and, therefore, contained varying percentages of oxides of nitrogen, along with traces of other impurities peculiar to this process.

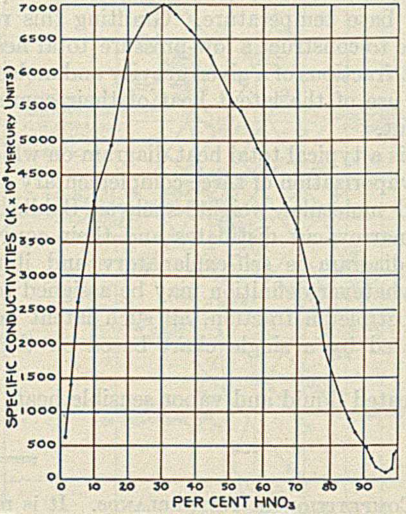


Figure 2. Electrical Conductivities of Nitric Acid

Veley and Manley curve, *3*

These results, when plotted, using ohms resistance as ordinates and acid strengths as abscissas, gave a curve (Figure 5) which indicated values as a method by which cuts could be made at definite acid concentrations.

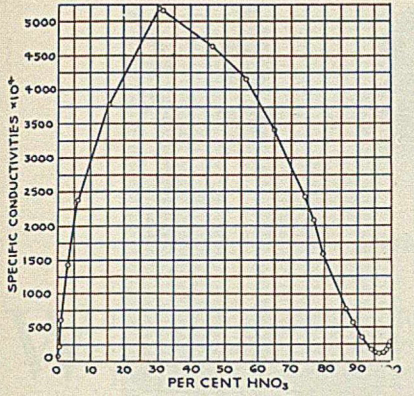


Figure 3. Electrical Conductivities of Nitric Acid at 28° C.

Author's curve; cell constant, 0.45

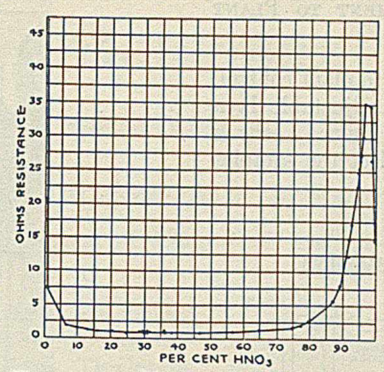


Figure 4. Nitric Acid Concentration *vs.* Ohms Resistance at 28° C.

Cell constant, 0.45

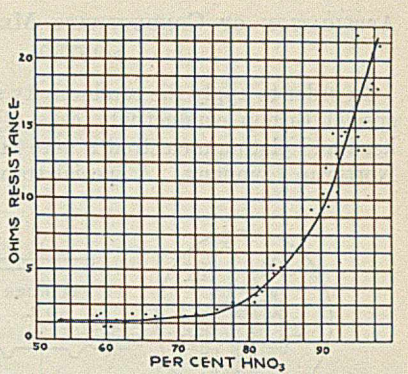


Figure 5. Nitric Acid Concentration *vs.* Ohms Resistance

Samples drawn from the process of manufacturing nitric acid from Chile saltpeter and measured with laboratory cells at 28° C.

There were, however, a few values for strong nitric acid known to contain a high percentage of oxides of nitrogen which did not fall exactly on the curve, but, since the oxides distill over first and along with the strong acid, they are out of the way before the nitric acid concentration falls below 90 per cent and, therefore, do not militate against the practical value of the curve. Nitric acid containing both oxides of nitrogen and chlorine, and nitric acid containing only oxides of nitrogen, when measured gave practically the same difference in conductivity readings taken before and after air-blowing; this indicates that the inflection of the points on the curve was caused entirely by the presence of oxides of nitrogen. Interest of a general nature led to the investigation of this influence of oxides of nitrogen on the conductivity of nitric acid.

In the investigation, samples from the process were drawn into 8-gallon stoneware crocks which were placed in a warm room and blown with air until the oxide content had been reduced to zero. Analysis and conductivity checks were made daily. It was interesting to observe the building up in acid concentration of the samples so long as there were oxides of nitrogen present, and the more or less rapid falling off in concentration as soon as all the oxides of nitrogen had been dispelled.

Oxides of nitrogen increase the conductivity of nitric acid. Much time was required and a large number of samples investigated before sufficient data could be collected to measure properly this conductivity increase. These values plotted in terms of both nitric acid and oxides of nitrogen concentration (Figure 6) supply all the corrections necessary for oxides of nitrogen up to 3.5 per cent. Although the data as plotted list only tests on nitric acid concentration between 90 and 100 per cent, there were some tests made on acids of lower concentration containing oxides of nitrogen, but in these the oxides of nitrogen did not appear appreciably to affect the conductivity. The influence of oxides of nitrogen is, therefore, concentrated in a small area and thus has a minimum effect on the utility of analysis by this method since a conductance minimum between 96 and 97 per cent already precludes the use of any values above this concentration.

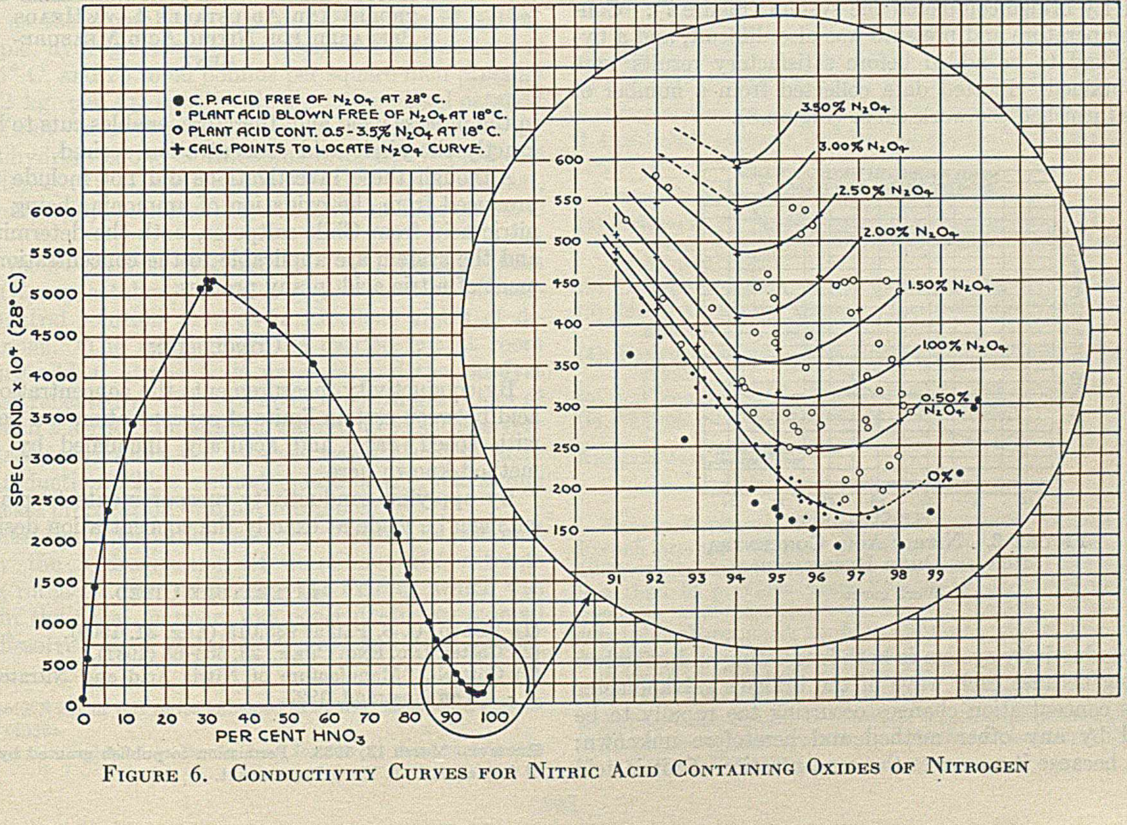


Figure 6. Conductivity Curves for Nitric Acid Containing Oxides of Nitrogen

Application of Conductivity Measurement to Plant Control

In order to apply the conductivity system to plant control, special Bishop conductivity cells (*1*) with adjustable lava head and platinum electrodes were furnished by the Leeds & Northrup Company. A special trap to collect the samples and also act as a reservoir for the cells was developed with the aid of the Duriron Company. The standard cells as installed were charged with approximately 70 per cent nitric acid because of the high boiling point of this concentration. A water jacket around the trap and a Leeds & Northrup conductivity bridge completed the system (Figure 7). Control of temperature and pressure was also difficult, and a by-pass line had to be added before satisfactory results were finally obtained. Plotted data collected from a number of test runs furnished the work curve (Figure 8).

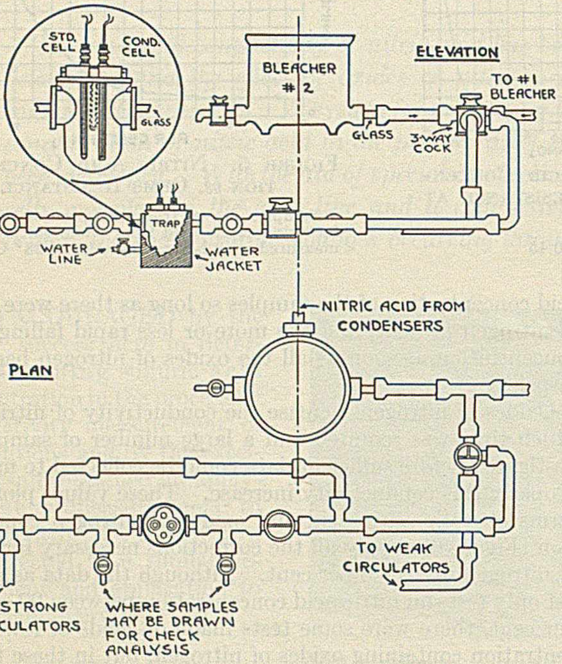


Figure 7. Flow Sheet of System

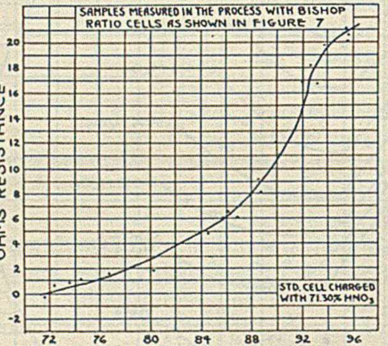
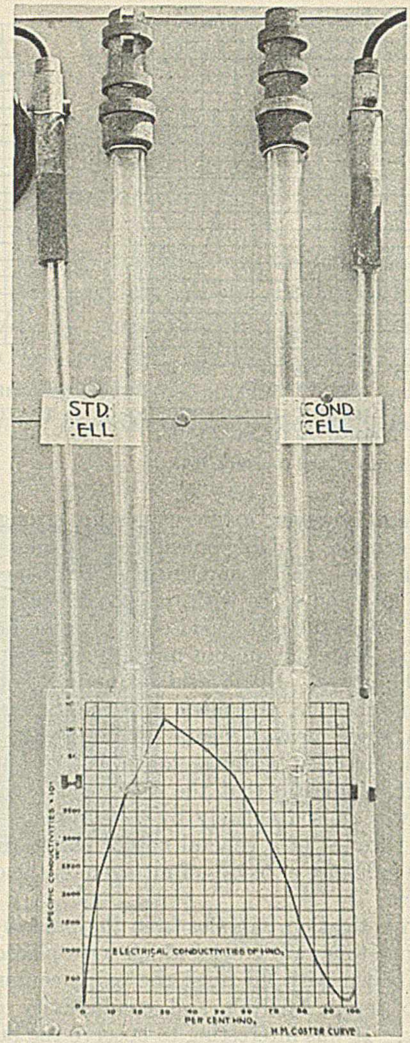


Figure 8. Nitric Acid Concentration *vs.* Ohms Resistance

Work curve



Leeds & Northrup Special Conductivity Cells with Platinum Electrodes and Adjustable Lava Heads Prepared for Nitric Acid Measurement

This conductivity system is both interesting and effective: interesting because each wave of the bridge's galvanometer indicates concentration changes occurring too rapidly to be observed by any other method and heretofore unknown; effective because it measures the concentration of nitric acid in the process itself and, therefore, enables cuts to be made at exactly the nitric acid concentration desired.

Although these investigations did not include nitric acid produced from the oxidation of ammonia, being limited to nitric acid from Chile saltpeter, both the determined values and the system are applicable to the concentration measurement of nitric acid in any process.

Conclusion

By conductivity measurements the concentration of nitric acid between certain limits of concentration can be measured with speed, ease, and accuracy unequaled by any other method known here.

By applying conductivity measurements to plant control cuts can be made at exactly the concentration desired.

Literature Cited

(1) Bishop, U. S. Patent 933,015 (Aug. 31, 1909).
(2) Coster, Ind. Eng. Chem., 23, 563–65 (1931).
(3) Cottrell, "Manufacture of Nitric Acid and Nitrates," p. 338, Van Nostrand, 1923.

Received March 13, 1933. Permission to publish granted by the Bureau of Ordnance, U. S. Navy Department.

Rotenone

XXVIII. Preparation of Dihydrorotenone[1]

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When rotenone is applied to foliage as an insecticide, it is gradually oxidized to inert compounds, especially on exposure to direct sunlight. This loss in toxicity is a considerable disadvantage for large-scale operations.

Of the large number of rotenone derivatives which have been tested against insects, all have been found to be relatively nontoxic with the exception of dihydrorotenone which equals or surpasses rotenone itself as an insecticide. This derivative appears also to be considerably more stable to oxidation when exposed on foliage than is rotenone (*3*). Therefore a method whereby dihydrorotenone may be obtained conveniently in good yield is of considerable practical importance.

Dihydrorotenone is formed on hydrogenation of rotenone with palladium barium sulfate or platinum oxide catalyst in acetone or ethyl acetate solution (*4*). With either catalyst in neutral solution in addition to dihydrorotenone, variable quantities of the relatively nontoxic rotenonic acid are formed (*5*). The use of platinum or palladium catalysts is too expensive when large quantities of dihydrorotenone are to be produced; moreover, with these catalysts a considerable proportion of rotenone is reduced to the relatively nontoxic rotenonic acid.

Among the catalysts that suggest themselves is nickel. This is inexpensive and extensively used commercially for the saturation of double bonds. However, a molecule possessing such a complicated structure as rotenone may give products other than the desired dihydrorotenone with different nickel catalysts, as these catalysts vary in their mode of action. For example, hydrogenation of rotenone in butyl acetate at 95° to 105° C. and 25 to 60 pounds per square inch pressure (1.8 to 4.2 kg. per sq. cm.)[2] with an active nickel catalyst prepared from oxidized nickel wool, turnings, or wire (*1*) gave no dihydrorotenone or rotenonic acid, but it produced dihydrorotenol (*6*) in quantitative yields. This product, like rotenonic acid, is considerably less toxic to insects than is rotenone.

With a nickel catalyst prepared from a nickel-aluminum alloy (*2*) (Raney catalyst), however, hydrogenation of rotenone in neutral solution resulted in excellent yields of dihydrorotenone. The reaction can be carried out at room temperature and at atmospheric pressure, and the catalyst can be used repeatedly. For example, when 10-gram lots of rotenone with 2.5 grams of catalyst were reduced successively in ethyl acetate solution, the catalyst was still active after the tenth reduction. This method should be a practical one for large-scale preparation of dihydrorotenone.

It was also found that dihydrorotenone could be obtained readily by the hydrogenation of derris or cubé extracts containing rotenone. In these cases the extract, which was prepared in the usual manner, was concentrated to a small volume, dissolved in a suitable solvent, and then hydrogenated.

Experimental Procedure

All the hydrogenations of rotenone were carried out at 35° to 40° C. under atmospheric pressure, and at a concentration of 5 to 10 per cent. The solvents used were benzene, ethyl acetate, butyl acetate, and acetone. The solution of rotenone was placed in the reaction bottle of a Burgess-Parr catalytic reduction apparatus, and the catalyst was added. The quantity of catalyst can be varied over a wide range without altering the final products. The apparatus was evacuated and then filled with hydrogen, and the mixture was shaken until one mole of hydrogen had been absorbed. The solution was then decanted from the solvent, filtered, and concentrated to a small volume. A suitable quantity of 95 per cent ethyl alcohol was then added. The crystals which deposited were in most cases pure dihydrorotenone. The yield of dihydrorotenone was: In benzene, 90 to 93 per cent; in ethyl acetate, 85 to 90; in butyl acetate, 85 to 90; in acetone, 60 to 70. In the case of acetone, 30 to 40 per cent of rotenonic and dihydrorotenonic acids were formed.

For the preparation of dihydrorotenone from plant extracts containing rotenone, the following procedure was used: When ether was used for extracting the root, the extract was concentrated to a thick sirup. This sirup was then dissolved in a suitable solvent and hydrogenated until the absorption of hydrogen had practically ceased. When acetone was used as the extracting solvent, the extract was concentrated to a suitable volume and the solution was hydrogenated until there was no longer an appreciable absorption of hydrogen. Hydrogenation in ethyl acetate of an ether extract of cubé root, which assayed 8.6 per cent rotenone, gave 7 per cent dihydrorotenone; an acetone extract of another aliquot of the same root yielded 8.2 per cent dihydrorotenone. The hydrogenation of an acetone extract of derris root containing 1.4 per cent rotenone yielded one per cent dihydrorotenone.

Literature Cited

(1) Bolton, E. R., British Patent 162,370 (April 26, 1921); Technical Research Works, Ltd., and Lush, E. J., British Patent 203,218 (Sept. 6, 1923).

(2) Covert and Adkins, *J. Am. Chem. Soc.*, 54, 4116 (1932).

(3) Jones, Gersdorff, Gooden, Campbell, and Sullivan, *J. Econ. Entomol.*, 26, 451 (1933).

(4) Kariyone, Kimura, and Kondo, *J. Pharm. Soc. Japan*, 43, 10 (1923).

(5) LaForge and Smith, *J. Am. Chem. Soc.*, 51, 2578 (1929).

(6) LaForge and Smith, *Ibid.*, 51, 2580 (1929).

Received June 7, 1933.

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[1] Parts I to XXVII of this series appeared in *J. Am. Chem. Soc.*, Vols. 51 (1929) to 55 (1933).

[2] The authors are indebted to Derris, Inc., for having these experiments made.

French Chemical Notes. The Société St. Gobain, a leading French producer of glass and chemicals, in its recent report on 1932 results stated that demand for sulfuric acid was appreciably less than in previous years because of decreased deliveries of domestic superphosphate to French farmers. The acid and superphosphate plant in Marennes was closed and the trade transferred to a plant in Tonnay.

Sales of nitrogenous fertilizers during 1932 were comparatively good, and a new plant was opened in Rouen in addition to the sodium nitrate factory in Chauny, which commenced production in March as a joint operation of the St. Gobain and the Société de la Grande Paroisse.

Evaporation by Submerged Combustion

I. Experimental Equipment

KENNETH A. KOBE, FRANK H. CONRAD, AND EINAR W. JACKSON
Department of Chemical Engineering, University of Washington, Seattle, Wash.

Experimental equipment has been constructed for the evaporation of liquids by submerged combustion. The equipment is constructed of metal and is of such a size that development-scale results can be obtained. The evaporation of water has been carried out in this apparatus with thermal recoveries of 95.2 and 91.2 per cent. With the use of this equipment the concentration of liquids which are corrosive or offer other difficulties in the usual type evaporator has been carried out with the same high efficiency as the evaporation of water alone.

SUBMERGED combustion is a method of heating a liquid by direct contact of the flame from a burner which projects the hot gases of the flame directly into and at any depth below the surface of the liquid.

Since 1886 workers have attempted to cause combustion to take place in the steam boiler where heat transfer from the hot gases of the combustion to the liquid could take place without having a separating metal wall. The advantages of such a process are numerous. The intimate contact of the hot gases and the liquid brings about thermal equilibrium between them; in fact, efficiencies of 106.2 per cent of the net or 94.5 per cent of the gross heating value are reported for gaseous fuels (*2*). Since the walls of the containing vessel are no longer used for heat transfer, their temperature is only that of the contained liquid. This prevents the deposition of scale from salts that have an inverted solubility curve, such as calcium sulfate. Corrosion is also minimized and the vessel may be constructed of alloys or ceramic ware to prevent attack.

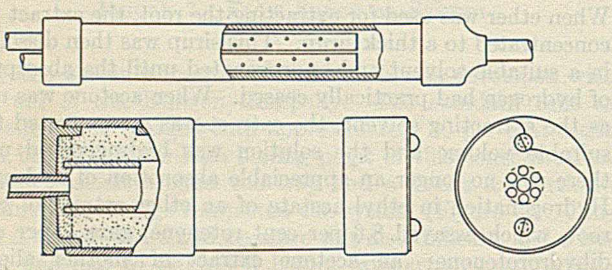

FIGURE 1. MIXING CHAMBER (ABOVE) AND BURNER

The many advantages of submerged combustion led to the construction of an experimental apparatus which has been used for the evaporation of sulfite waste liquor and other materials which are evaporated with difficulty by the usual methods. The calculations of results from the test data make it a desirable experiment for stoichiometric calculations on combustion.

CONSTRUCTION OF BURNER

The principles employed in the construction of submerged combustion apparatus have been previously discussed (*3*). The construction of a burner using gaseous fuel consists of three essential parts: (1) a mixing chamber which will produce a homogeneous gas-air mixture, (2) a velocity tube through which the gas-air mixture flows at a rate greater than the rate of flame propagation, and (3) a combustion chamber containing a refractory surface which becomes incandescent and acts as an ignition point for the gas-air mixture.

The construction of the burner parts is shown in Figure 1 and utilizes standard pipe fittings for all parts. The mixing chamber consists of a $^3/_4$-inch (1.9-cm.) pipe, 8 inches (20.3 cm.) long. It contains two pieces of $^3/_8$-inch (0.95-cm.) copper tubing 8 inches long; one end of each tube is sealed off and $^1/_{32}$-inch (0.8-mm.) holes drilled in a staggered arrangement from the sealed end to within 3 inches (7.6 cm.) of the open end. The tubes are then set into the $^3/_4$-inch pipe, the open ends extending about 2 inches (5.1 cm.) beyond the mixing chamber proper as inlets for gas and air, respectively. The copper tubes are soldered in holes drilled in the cap over the upper end of the mixing chamber. The mixing chamber is connected to the combustion chamber (Figure 1) by a velocity tube which consists of a 2-foot (61-cm.) (or any suitable length) piece of standard $^1/_8$-inch (0.32-cm.) pipe. The combustion chamber casing is made from a 2-inch pipe, 5 inches (12.7 cm.) long. The upper end is threaded into a coupling which has a plug drilled and threaded to receive the velocity tube. The lower end of the pipe is closed with a cap in the center of which is drilled a one-inch (2.5-cm.) hole. The refractory tube is a one-inch combustion tube of fused silica. The tube is held in place at each end with a refractory cement (such as Smooth-On). The annular space between the combustion tube and the pipe is filled with a suitable insulating material, such as diatomaceous earth. The end cap is drilled and threaded to receive two $^3/_{16}$-inch (0.48-cm.) screws which hold in place the grid. This is a $^1/_{16}$-inch (0.16-cm.) plate in which are

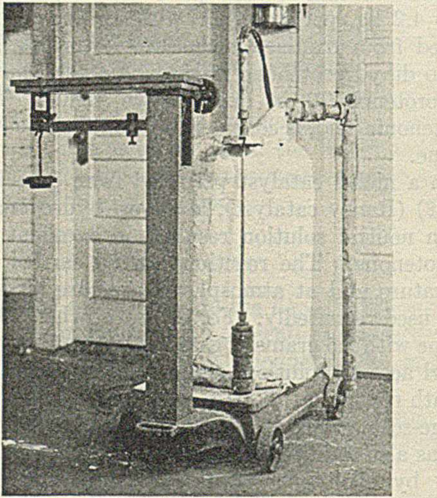

FIGURE 2. EVAPORATOR AND BURNER

drilled a number of $^3/_{16}$-inch holes in a position over the end of the combustion tube. The purpose of this grid is to break up the hot combustion gases into fine bubbles to facilitate heat transfer, thus decreasing the depth to which the burner must be submerged.

CONSTRUCTION OF EVAPORATOR

The first evaporator used consisted of a sheet metal cylinder, inside diameter 13 inches (33 cm.), and depth 25 inches (63.5 cm.). It has a clean-out also used as a thermometer well at the bottom and at the top, a $2^1/_2$-inch (6.4-cm.) opening for the burner, and a 2-inch pipe connection for exit gases. It is covered with 2 inches of asbestos-magnesia insulation. Figure 2 shows the burner and evaporator. Figure 3 shows a recently constructed evaporator. It is of sixteen-gage black iron, welded construction, diameter 12 inches (31 cm.), depth of body 18 inches (45.8 cm.), depth of cone bottom 12 inches. The cover is removable and has a 4-inch (10.2-cm.) opening for the burner and two 2-inch pipe couplings for gas removal and feed entrance. The cone bottom ends in a threaded 2-inch pipe on which is screwed a cock or gate valve.

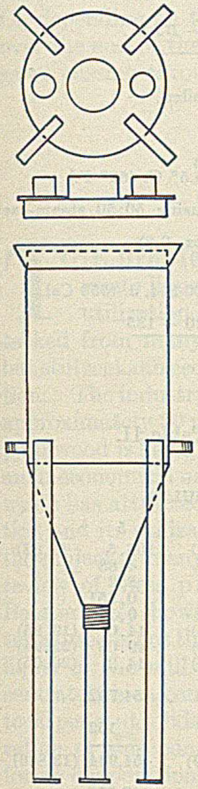

FIGURE 3. EXPERIMENTAL EVAPORATOR BODY

OPERATION OF BURNER

Carbureted water gas produced by the Seattle Gas Company is used as fuel. It is necessary to increase the gas pressure from the gas main pressure of 3 inches (7.6 cm.) of water to approximately 6 inches (15.3 cm.) of mercury (about 3 pounds per square inch or 211 grams per sq. cm.). This is accomplished by a small, fin type, rotary compressor. The gas is passed to a storage tank to eliminate fluctuations in pressure, through a needle valve, a standard orifice meter and then to the burner.

Air is taken from the building compressed-air line at a pressure of 40 pounds per square inch (281 grams per sq. cm.) through a needle valve, a standard orifice meter, and then to the burner. The volumes of gas and air are indicated by the manometer of the orifice meters so that the air-gas ratio can be maintained constant. The burner is connected to the gas and air nipples with rubber tubing.

To light the burner, it is removed from the evaporator, the grid over the burner nozzle moved to one side, the gas turned on and lighted. The air is then turned on until the correct air-gas ratio is obtained. Combustion takes place at the end of the combustion tube; thus, it is necessary to move the flame back into the tube so combustion will take place within the combustion chamber. This is done by inserting an incandescent piece of iron wire into the combustion chamber. The combustion tube is soon heated to incandescence and acts as a hot spot for the ignition of the gas as it leaves the velocity tube. The metal grid is then returned to its position over the end of the burner and the burner is ready to submerge.

EVAPORATION OF WATER

The charge to be evaporated is put into the evaporator; the lighted burner is placed in position and throughout the run is adjusted so as to remain completely submerged. The burner is kept submerged to such a depth that thermal equilibrium exists between the liquid and vapors, as indicated by thermometers in the liquid and vapor. The evaporator is placed on scales so that the rate of evaporation is determined by weighing at intervals of time. The experimental data taken in two runs on water are given in Table I as average values of a series of readings.

TABLE I. EXPERIMENTAL DATA

Run	4		5	
Time of run, min.	180		177	
Barometer, mm. Hg	755		756.5	
Static pressure of gas, inches Hg	4		6	
Static pressure of gas, mm. Hg	101.6		152.4	
Temp. of gas entering, ° C. (° F.)	22.8	(73)	22.8	(73)
Pressure, gas Venturi:				
Inches (mm.) C_6H_6 (1:10)	2.54	(64.5)	4.34	(110.2)
Inches (mm.) H_2O	7.34	(186.4)	8.15	(207.0)
Room temp., ° C. (° F.)	23	(73)	26	(79)
Skin temp. of evaporator, ° C. (° F.)	26	(79)	31	(88)
Weight H_2O:				
Used, lb. (kg.)	68.5	(31.07)	67.5	(30.62)
Evaporated, lb. (kg.)	34.5	(15.65)	44.0	(19.96)
Temp. H_2O in evaporator, ° C. (° F.)	87.5	(189.5)	88.2	(190.8)
Temp. of vapor, ° C. (° F.)	92.3	(198.2)	90.6	(195.0)
Exit gas analysis:				
CO_2	10.1		12.4	
O_2	3.6		1.6	
N_2	86.3		86.0	
Fuel gas analysis:				
CO_2	5.4		..	
Illuminants (C_3H_6)	7.1		..	
O_2	0.3		..	
CO	11.4		..	
H_2	27.0		..	
CH_4	20.2		..	
C_2H_6	0.7		..	
N_2	27.9		..	
Fuel gas, B. t. u./cu. ft. (cal./cu. m.)	505	(4494)		

NOTE: Unless otherwise indicated, cubic feet are at 60° F., 30 inches Hg, and saturated with water. Heating value of fuel gas taken at 505 B. t. u./cu. ft., the value given by the gas company. Illuminants are considered to be entirely propylene.

CALCULATION OF RESULTS

Knowing the analysis of the fuel gas and of the exit gas, it is possible to make use of stoichiometric relationships to calculate efficiencies and check experimentally determined values. Sample calculations for run 4 are as follows:

(Basis, one mole fuel gas)

COMPONENT		C	H_2	O_2 REQUIRED FOR COMBUSTION
	Mole	*Atom*	*Mole*	*Mole*
CO_2	0.054	0.054	...	...
Illuminants (C_3H_6)	0.071	0.213	0.213	0.319
O_2	0.003	...	...	−0.003
CO	0.114	0.114	...	0.057
H_2	0.270	...	0.270	0.135
CH_4	0.202	0.202	0.404	0.404
C_2H_6	0.007	0.014	0.021	0.025
N_2	0.279	...	...	...
	1.000	0.597	0.908	0.937

(Basis, 100 moles dry exit gas)

COMPONENT		C	O_2
	Moles	*Atoms*	*Moles*
CO_2	10.1	10.1	10.1
O_2	3.6	..	3.6
N_2	86.3	..	..
	100.0	10.1	13.7

Moles fuel gas used:

$$\frac{10.1}{0.597} = 16.9 \text{ moles fuel gas used per 100 moles exit gas}$$

Oxygen balance:

$$0.279 \times 16.9 = 4.7 \text{ moles } N_2 \text{ from fuel gas}$$

$$86.3 - 4.7 = 81.6 \text{ moles } N_2 \text{ from air}$$

$$81.6 \times \frac{0.21}{0.79} = 21.7 \text{ moles } O_2 \text{ from air}$$

$$21.7 - 13.7 = 8.0 \text{ moles } O_2 \text{ disappeared by combining with } H_2$$

Air-gas ratio:

$$\frac{81.6}{0.79 \times 16.9} = 6.11 \text{ moles air admitted per mole fuel gas}$$

Excess air:

$$\frac{3.6 \times 100}{16.9 \times 0.937} = 22.7\% \text{ excess air}$$

From the calibration curve of the gas orifice meter the data for run 4 show that 80.2 cu. ft. (2.27 cu. m.), or 0.207 mole, of fuel gas were used during the run.

Basis, 0.207 mole fuel gas:

$2 \times 8.0 \times \frac{0.207}{16.9} = 0.196$ mole H_2 burned (from O_2 balance)

$0.207 \times 0.908 = 0.188$ mole H_2 entered (from gas analysis)

WATER BALANCE.

Water formed by combustion:

$0.207 \times 0.908 \times 18 = 3.38$ lb. (1.53 kg.) H_2O formed by combustion

We can assume the gas and air used are saturated with water vapor at 60° F. (15.5° C.).

$0.207 \times 6.11 = 1.26$ moles air enter with gas

Water in gas and air:

$(0.207 + 1.26) \times \frac{13}{755 - 13} \times 18 = 0.46$ lb. (0.21 kg.) H_2O enter in gas and air

Total water leaving evaporator:

$34.5 + 3.38 + 0.46 = 38.34$ lb. (17.39 kg.) H_2O leave evaporator

Since the total pressure is the sum of the partial pressures of the water vapor and gaseous products of combustion, a check on the data and calculations can be obtained. The vapor pressure of water at 87.5° C. is 478 mm. mercury.

Partial pressure of gases:

$755 - 478 = 277$ mm.

Water that should have been evaporated:

$100 \times \frac{478}{277} \times \frac{0.207}{16.9} \times 18 = 38.1$ lb. (17.28 kg.) H_2O should have been evaporated

HEAT BALANCE.

Heating value of fuel gas:

$80.2 \times 505 = 40{,}501$ B. t. u. (10,206 Cal.)

Sensible heat (from Eastman's curves, *1*) per mole of gas and air entering (sensible heat of gas assumed to be that of air).

	moles	at 73° F. (22.8° C.)		at 60° F. (15.5° C.)		difference	total
Gas + air	1.467	286	−	194	=	92	135 B. t. u. (34 Cal.)

Heat of vaporization of water evaporated:

$34.5 \times 983.7 = 33{,}938$ B. t. u. (8552 Cal.)

Heat of vaporization of water from combustion:

$3.38 \times 983.7 = 3325$ B. t. u. (838 Cal.)

Composition of exit gases:

$\frac{0.207}{16.9}(3.6 + 86.3) = 1.10$ moles $O_2 + N_2$

$\frac{0.207}{16.9} \times 10.1 = 0.12$ mole CO_2

$\frac{38.34}{18} = 2.13$ moles H_2O

Sensible heat per mole in exit gases:

	moles	at 198.2° F. (92.3° C.)		at 60° F. (15.5° C.)		difference	total
CO_2	0.12	1600	−	260	=	1340	162
$O_2 + N_2$	1.10	1175	−	195	=	980	1078
							1239 B. t. u. (212 Cal.)

Superheat of water vapor:

	moles	at 198.2° F. (92.3° C.)		at 189.5° F. (87.5° C.)		difference	total
H_2O	2.13	1410	−	1330	=	80	170 B. t. u. (42.8 Cal.)

HEAT INPUT.

Heating value of gas = 40,501
Sensible heat of gas and air above 60° F. = 135
40,636 B. t. u. (10,249 Cal.)

HEAT OUTPUT.

Heat of vaporization of water evaporated = 33,938
Heat of vaporization of water from combustion = 3,325
Sensible heat in gases, above 60° F. = 1,239
Superheat of water vapor = 170
Thermal recovery = 38,672
Radiation and unaccounted for losses = 1,964
40,636 B. t. u. (10,249 Cal.)

Thermal efficiency (percentage of heat input recovered in products):

$$\frac{38{,}672}{40{,}636} \times 100 = 95.2\%$$

Evaporation efficiency (percentage of heat input used to evaporate contained water):

$$\frac{33{,}938}{40{,}636} \times 100 = 83.6\%$$

Over-all efficiency:

Making use of the Swindin formula (*4*), we can calculate the over-all efficiency, accounting for the work done on the gas and air by the compressors:

$$E = \frac{H_1 + H_2 - \frac{AJ}{E_i \times E_e \times E_c} - BJ}{H_o}$$

where E = efficiency of submerged combustion boiler
H_1 = heat in steam
H_2 = heat in products of combustion
H_o = heat in fuel
A = work done in compressing air and gas
B = work contained in gas on cooling to 15.5° C. (60° F.)
J = Joule's mechanical equivalent of heat
E_i = thermodynamic efficiency of engine using 50:50 steam-gas mixture (approx. 0.16)
E_e = mechanical efficiency of engine (approx. 0.8)
E_c = efficiency of compressor (approx. 0.7)

$$\frac{AJ}{E_i \times E_e \times E_c} = \frac{1.5 \times 1.99 \times 533}{0.16 \times 0.8 \times 0.7} \ln \frac{34}{30} = 2220 \text{ B. t. u. (559 Cal.)}$$

$$E = \frac{(33{,}938 + 3325 + 170) + 1239 - 2220 - 135}{40{,}501}$$

$$= \frac{36{,}317}{40{,}501} \times 100 = 89.7\%$$

The results from runs 4 and 5 are given in Table II.

TABLE II. CALCULATED RESULTS

Run	4		5	
Gas used, cu. ft. (cu. m.)	80.2	(2.27)	106.5	(3.02)
Ratio air to gas	6.11		4.88	
Excess air, %	22.7		8.2	
H_2 in gas used, mole	0.188		0.251	
H_2 calcd. by O_2 balance, mole	0.196		0.194	
H_2O evaporated (weighed), lb. (kg.)	34.5	(15.65)	44.0	(19.96)
H_2O output, lb. (kg.)	38.34	(17.39)	49.03	(22.24)
Calcd. H_2O output, lb. (kg.)	38.1	(17.28)	44.2	(20.05)
Heating value of gas	40,501		54,792	
Sensible heat of gas and air above 60° F.	135		152	
Heat input, B. t. u. (Cal.)	40,636	(10,249)	54,944	(13,846)
Heat of vaporization of H_2O evaporated	33,938		43,252	
Heat of vaporization of H_2O from combustion	3,325		4,797	
Sensible heat in gases above 60° F.	1,239		1,345	
Superheat of H_2O vapor	170		136	
Thermal recovery	38,672		49,530	
Radiation and unaccounted for losses	1,964		5,414	
Heat output, B. t. u. (Cal.)	40,636	(10,249)	54,944	(13,846)
Efficiency, %:				
Thermal	95.2		91.2	
Evaporation	83.6		80.3	
Over-all	89.7		84.4	

DISCUSSION OF RESULTS

The results in Table II show that submerged combustion evaporation has a high thermal efficiency. This is due to the fact that the outer wall of the evaporator is at the temperature of the liquid and not at the higher temperature of the medium supplying the necessary heat. The evaporation efficiency is much lower, as the water produced in the combustion of the gas must also be evaporated. The efficiency is calculated on the basis of the total heat supplied and not as the basis of the net heating value of the gas, or that heat ordinarily available when the water of combustion cannot be condensed.

It may be seen that the method of submerged combustion evaporation will not compete with the usual type of multiple-effect evaporation, except for those substances which offer unusual difficulties, such as highly corrosive solution, highly viscous solution, and scale- or sludge-forming solutions. These latter solutions can be handled very well with submerged combustion evaporation at high efficiency and without the difficulty attached to heat transfer through tubes.

The stoichiometric calculations of run 4 check well, but those of run 5 do not show as good agreement; errors in gas analysis can readily cause all these calculations to show discrepancies.

Fused silica is not a satisfactory refractory material as it devitrifies at about 1200° C., and the temperature within the combustion chamber is practically equal to the theoretical flame temperature of the gas, or about 2000° C. Thus the temperature of the refractory walls is at least 1400° to 1700° C., depending on the operating conditions. The metal grid over the end of the burner is slowly burned away by the hot gases passing through, but it can easily be replaced. With these exceptions there has been no noticeable deterioration of the burner or evaporator parts, even when normally corrosive solutions were evaporated.

Acknowledgment

The writers wish to thank W. L. Beuschlein for his helpful suggestions and interest in this work.

Literature Cited

(1) Eastman, Bur. Mines, *Tech. Paper* 445 (1929).
(2) Hammond, *J. Inst. Fuel*, 3, 303 (1930).
(3) Kobe and Hauge, *Power*, 77, 402 (1933).
(4) Swindin, *Trans. Inst. Chem. Eng.* (London), 5, 132 (1927).

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II. Sulfite Waste Liquor

Unneutralized sulfite waste liquor has been successfully evaporated by submerged combustion without the difficulties encountered by the usual tube type evaporators. The evaporation gives a product containing 63.4 per cent solids, with a thermal recovery in the process of approximately 94 per cent. Higher concentrations of solids can be obtained.

In order to form a thermal cycle in recovery, evaporation, and combustion of the sulfite waste liquor, the present pulp mill practice must be changed to give a waste liquor of over 12 per cent solids. Below this concentration the evaporation will require more heat than is recovered by the combustion of the solid residue.

The application of the principles of submerged combustion offers a technical and economic solution to the problem of sulfite waste liquor disposal.

THE problem of sulfite waste liquor disposal or utilization has been attacked from many standpoints but still seeks an economical solution. The industry realizes that approximately 50 per cent of the pulp wood is being disposed of in an uneconomical manner. This waste has attracted much attention and its utilization has been the subject of many patents. A review of these proposals by Benson (*3*, *4*) shows that the material used is not the dilute waste liquor of the mill but is a concentrate which contains from 50 to 90 per cent solids. The preparation of this concentrate calls for an evaporation process.

Sulfite waste liquor has been a pollution nuisance because no utilization has been made on a scale large enough to consume the entire supply of waste liquor. The result is that disposal by dumping in the nearest body of water has been the common practice. This has not gone on without objection from neighboring cities or industries who have forced the mills to use a less objectionable method of disposal. The usual method has been concentration and combustion of the organic solids. Since a concentration to at least 50 per cent solids is necessary previous to combustion, an evaporation process is usually employed.

Evaporation of Sulfite Waste Liquor

The evaporation of sulfite waste liquor in tube evaporators has been the subject of considerable research and has been employed on a commercial scale. The difficulties in the evaporation have been pointed out by Badger (*2*) and by Miller (*9*). These are: (1) the extreme viscosity of the solution, (2) the serious scale-forming tendencies of the liquor, (3) the corrosive nature of the unneutralized liquor, (4) excessive foaming, and (5) the escape of volatile substances causing trouble in condensing.

Badger (*2*) carried out his work on neutralized liquor to avoid corrosion difficulties. Forced circulation was necessary with the viscous solution, and high values of the heat transfer coefficients were obtained in this way. No scale deposit was found on the nickel tubes. Miller (*9*) used neutralized liquor in an evaporator with heating rings, which gave natural circulation. The cylindrical surfaces of the heating rings are mechanically cleaned of scale by a scraper continuously operating between the rings. The Paulson method (*3*) employs a double-effect, stainless-steel evaporator, operated under a pressure of 180 pounds per square inch in the first effect and 130 pounds per square inch in the second effect. The pressure operation prevents foaming and allows the steam from the second effect to be utilized for pulp cooking. The concentrated liquor from the first effect is burned in a Wagner furnace for the production of steam to heat the first effect. This arrangement is equivalent to the installation of a new and expensive steam-generation system in plants already possessing adequate steam plants. Kuhles (*8*) has described a plant in which the waste liquor is first evaporated in multi-effect evaporators from 10–12 per cent solids to 40–50 per cent solids, then spray-dried to 5–8 per cent moisture. This dried residue is a fine powder which can be burned in a powdered coal burner.

Despite the numerous systems proposed and described as operating successfully, it is also known that some such plants have failed (*1*), and that others do not continuously operate with the freedom from difficulty that their sponsors have described. With hopes of overcoming these difficulties the concentration of sulfite waste liquor by submerged combustion has been attempted on an experimental scale (*5*).

Submerged Combustion Evaporation

The concentration of sulfite waste liquor by submerged combustion eliminates many of the difficulties inherent in the tube evaporator. As previously pointed out (*7*), whenever heat is transferred through a metal wall, corrosion and scale formation take place. With a submerged combustion burner the heat transfer is directly between the hot gases and the liquid so that the formation of solid calcium sulfate at the interface now merely results in its precipitation in the liquid. The body of the evaporator is at the same temperature as the liquid, and, since it is not externally heated, corrosion is slight or may be resisted by alloys or ceramic ware. These numerous advantages of submerged combustion make it appear to be a promising method of attack on this problem.

EXPERIMENTAL PROCEDURE

The equipment used for submerged combustion evaporation has been described in Part I (*6*).

SULFITE WASTE LIQUOR. Waste liquor from the pulping of hemlock was drawn directly from the digestor before it was blown. Analysis showed the following composition:

Sp. gr.	1.059	Total solids, %	12.1
Free acid, %	0.4	Ash in solids, %	13.5
Total acid, %	0.6	Heating value of dry solids, B. t. u./lb.	9150

OPERATION. The evaporator was charged with unneutralized sulfite waste liquor and the lighted burner submerged in the liquid. When the temperature of the liquid had come to a constant boiling point, the data for the runs were taken. Evaporation took place with no difficulty. Despite the fact that gas was being introduced into the liquid, no foaming occurred. The free sulfur dioxide in the liquor was evolved at the beginning of the run.[1] No scale was found in the evaporator or on the burner itself. A small amount of carbonized material was found adhering to the metal grid near the openings for the hot gases, though the amount of material did not build up enough to interfere with the operation of the burner. From the initial weight of the evaporator and the loss in weight as evaporation occurred, the approximate concentration of solids could be calculated. Two runs (6 and 7) were made using the 12.1 per cent liquor in which the solids content was increased to approximately 33 per cent. The product from these two runs was then mixed and concentrated to 63.4 per cent solids. Further concentration could not be carried out in this run, as the depth of liquid in the evaporator became too low for operation of the burner in the liquid. Higher concentrations of solids could have been reached had larger amounts of sulfite liquor been concentrated in runs 6 and 7. The data for all runs are given in Table I.

TABLE I. EXPERIMENTAL DATA

Run	6	7	8
Time of run, min.	217	200	130
Barometer, mm. Hg	758	766	766
Static pressure of gas, inches Hg	6	6	6.5
Temp. of gas entering, ° C. (° F.)	22.8 (73)	22.8 (73)	22.8 (73)
ΔP, gas orifice, inches C_6H_6	3.93	3.79	3.62
ΔP, air orifice, inches H_2O	7.82	7.48	7.33
Room temp., ° C. (° F.)	24 (75.2)	25 (77)	25 (77)
Weight of liquor used, lb.	75.5	74.25	55
Initial concn. of solids, %	12.1	12.1	33
Final concn. of solids, %	33	33	63.4
Weight of water evaporated, lb.	46.0	41.75	30
Temp. of soln. in evaporator, ° C. (° F.)	89 (192.2)	89.2 (192.6)	89.5 (193.1)
Temp. of vapors, ° C. (° F.)	88.3 (191)	88.3 (191)	91.1 (196)
Exit gas analysis, %:			
CO_2	11.8	12.1	12.1
O_2	1.5	1.6	1.6
N_2	86.7	86.3	86.3
Fuel gas analysis, %:			
CO_2	5.4	..	..
Illuminants (C_3H_6)	7.1	..	..
O_2	0.3	..	..
CO	11.4	..	..
H_2	27.0	..	..
CH_4	20.2	..	..
C_2H_6	0.7	..	..
N_2	27.9	..	..
Fuel gas, B. t. u./cu. ft.	505	..	..

The data from Table I have been calculated to give a water and heat balance as previously shown (*6*). The calculated results are given in Table II.

THERMAL CYCLE

The present mill practice of blowing the digestor and washing the entire blow from the pit is satisfactory when the waste liquor is to be run directly into a body of water. If evaporation of the waste liquor is to be employed the practice of dilution must be abandoned. It is possible to withdraw most of the waste liquor from the blow pit, thus securing a liquor containing from 10 to 12 per cent solids, instead of about 3 per cent as given at present. Since concentrated waste liquor containing over 50 per cent solids can be used as a fuel, either alone or mixed with fuel oil, a certain amount of the heat employed in the evaporation can be recovered by the combustion of the concentrate. Thus a thermal cycle can be formed.

TABLE II. CALCULATED RESULTS

Run	6	7	8
Time at equilibrium, min.	150	160	120
H_2O output (weighed), lb.	35.0	39.75	28.75
Gas used, cu. ft.	84.7	90.3	67.2
Ratio air to gas	5.22	5.03	5.03
Excess air, %	8.1	8.4	8.4
H_2 in gas used, mole	0.199	0.212	0.158
H_2O calcd. by O_2 balance, mole	0.184	0.178	0.132
H_2O output, lb.	39.01	44.01	31.92
Calcd. H_2O output, lb.	40.0	41.3	30.7
Heating value of gas used	42,774	45,602	33,936
Sensible heat in gas and air above 60° F.	125	130	96
Heat input	42,899	45,732	34,032
Heat of vaporization of H_2O evaporated	34,374	39,031	28,218
Heat of vaporization of H_2O from combustion	3,516	3,751	2,787
Sensible heat in gases above 60° F.	1,151	1,191	853
Superheat of H_2O vapor	0	0	35
Thermal recovery	39,041	43,973	31,893
Radiation and unaccounted for losses	3,858	1,759	2,139
Heat output	42,899	45,732	34,032
Efficiency, %:			
Thermal	91.0	96.2	93.8
Evaporation	80.1	85.4	82.9
Over-all	84.3	89.5	86.3

We may consider the heating value of the dry solids to be 9150 B. t. u. per pound, the over-all efficiency 85 per cent, the temperature of the feed liquor 70° F., and evaporation to occur at 192° F. with a heat of vaporization of 982 B. t. u. per pound. The sludge of maximum dilution which will give a thermal cycle for the process is calculated.

$$S = \text{lb. solids in 100 lb. waste liquor}$$

$$\frac{(100 - S)(1104)}{(0.85)(9150)} = S$$

$$S = 12.5 \text{ lb. solids}$$

Thus if the mill wishes to regain the amount of heat equal to that used in the evaporation, it is necessary that liquor be recovered from the blow pit which has 12.5 per cent solids. Since this concentration of solids is at the upper limit of the usual 10 to 12 per cent solids in the liquor from the digestor, it is apparent that it will not usually be possible to regain all of the heat used in the evaporation process.

DISCUSSION OF RESULTS

The successful application of submerged combustion evaporation to the concentration of sulfite waste liquor has shown that this method surmounts the difficulties which confront the other evaporation processes. Scale formation, corrosion, foaming, and forced circulation present special problems not yet entirely solved in present practice. Submerged combustion evaporation successfully eliminates such problems. Although such an evaporation system does not have the evaporator economy of a multiple-effect system, its numerous other advantages make it worthy of consideration. The principles of submerged combustion can be applied in a different apparatus using cheaper fuel, and the result can well be a piece of equipment which is both technically and economically superior to present practice.

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[1] The evolution and recovery of sulfur dioxide is now being studied further.

LITERATURE CITED

(1) Allen, *Chem. & Met. Eng.*, **32**, 928 (1925).
(2) Badger, IND. ENG. CHEM., **19**, 677 (1927).
(3) Benson, "Chemical Utilization of Wood," Rept. Natl. Comm. Food Utilization, Dept. Commerce, 1932.
(4) Benson, *Pacific Pulp Paper Ind.*, **6**, No. 13, 19 (1932); *Paper Trade J.*, **95**, No. 20, 31 (1932).
(5) Kobe, *Paper Trade J.*, **95**, No. 3, 33 (1932).
(6) Kobe, Conrad, and Jackson, IND. ENG. CHEM., **25**, 984 (1933).
(7) Kobe and Hauge, *Power*, **77**, 402 (1933).
(8) Kuhles, *Ibid.*, **72**, 468 (1930).
(9) Miller, *Can. Chem. Met.*, **14**, 19 (1930).

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Efficiencies of Tar Oil Components as Preservative for Timber

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IN THE determination of the fungicidal powers of creosote oil fractions by the wood pulp method of Rhodes and Gardner, the use of pine pulp gives results consistent with those obtained when Norway spruce pulp is used. No one compound in coal-tar creosote oil is primarily responsible for its preservative power, although diphenyl appears to be slightly more toxic to fungi than any other single compound. The fractions from water-gas tar oil are much less effective as preservatives than are those from coal-tar creosote oil. The chlorine derivatives of phenol and creosols and of naphthalene are more toxic to fungi than are the compounds from which they are obtained.

This investigation is essentially a continuation of that of Rhodes and Gardner (*2*). In this earlier work a method was devised for measuring the fungicidal powers of wood preservatives by determining the minimum concentration of preservative required to prevent the growth of *Fomes annosus* in mechanical wood pulp. The conditions in this test resemble, in many respects, those under which the preservatives are actually used, so that the experimental results should be indicative of the results that may be expected in service. This method of testing was used in the present investigation also.

A possible criticism of the original method of Rhodes and Gardner is that the test material was mechanical wood pulp from Norway spruce, which is not commonly used for structural purposes. To determine whether or not the apparent efficiency of the preservative varies with the specific type of wood pulp used, parallel tests were made with creosote oil fractions as the preservatives, using Norway spruce and mechanical pine pulps. The mechanical pine pulp was obtained through the courtesy of the Forest Products Laboratory, Madison, Wis. The results were as follows:

OIL FRACTION	LIMITING CONCENTRATIONS[a] NORWAY SPRUCE PULP A		PINE PULP A	
	A	B	A	B
	%	%	%	%
5	0.8	1.0	0.6	0.8
7	0.6	0.8	0.6	0.8
9	0.6	0.8	0.6	0.8

[a] A, maximum concentration at which any growth of *F. annosus* occurs; B, minimum concentration at which no growth of *F. annosus* occurs.

It appears that within the limit of experimental error the results of the test do not depend upon the specific type of pulp used.

Several investigators in this field have made comparisons of the relative efficiencies of preservatives by determining the concentrations of the various preservative substances that are required to inhibit the growth of the wood-destroying fungi in a malt-agar medium, or the concentration required to kill the fungi in such medium. One such method has been described by Schmitz and others (*3*). This method is a convenient one, although the conditions of the test differ so markedly from those of actual service that, in some cases at least, the results may not be directly comparable with those that may be expected in practice.

A series of fractions from coal-tar creosote oil was tested by the methods of Schmitz and of Rhodes and Gardner. The results were as follows:

FRACTION	KILLING CONCENTRATION Method of Rhodes and Gardner	KILLING CONCENTRATION Method of Schmitz	RATIO
	% by weight of wood pulp	*% by weight of agar medium*	
1	0.9	0.03	30:1
2	0.7	0.03	23:1
3	0.55	0.03	18:1
4	0.7	0.03	23:1
5	0.9	0.03	30:1
6	0.7	0.03	23:1
7	0.9	0.05	18:1
8	1.3	0.05	26:1
9	1.5	0.08	21:1
10	2.7	0.15	18:1
Mixture	0.9	0.05	18:1

These results show that in the comparison of the preservative efficiencies of various fractions from coal-tar creosote oil the two methods give reasonably consistent results, although quantitatively the concentration required to kill *Fomes annosus* in an agar medium is much lower than that to prevent the growth of this organism in wood.

COAL-TAR COMPOUNDS

The material used in this series of tests was prepared from a typical coal-tar creosote oil that showed the following analysis:

TEMP. RANGE	PER CENT DISTILLED[a] (BY WEIGHT)
° *C.*	
0-210	1.2
210-235	14.3
235-270	20.8
270-315	20.5
315-355	20.2
Residue	21.0
Limpid point, ° C.	27
Sp. gr. (38/15.5° C.)	1.065
Tar acids, %	11.6
Tar bases, %	5.9

[a] Bulb distillation by A. S. T. M. method D246-27T.

Several gallons of this material were freed from tar acids and bases by repeated alternate extraction with a 10 per cent solution of sodium hydroxide and a 30 per cent solution of sulfuric acid. Two liters of the resulting "dead oil" were distilled from an iron still provided with a Hempel fractionating column, and the distillate was collected in ten approximately equal fractions, as follows:

FRACTION	DISTN. TEMP.	FRACTION	DISTN. TEMP.	FRACTION	DISTN. TEMP.
	° *C.*		° *C.*		° *C.*
1	184-210	5	260-290	8	310-320
2	210-225	6	290-300	9	320-340
3	225-240	7	300-310	10	340-385
4	240-260				

The preservative efficiency of each fraction and of a mixture of equal parts by volume of the separate fractions was then determined by the wood pulp method. The following results were obtained:

Fraction	Limiting Concn. %	Fraction	Limiting Concn. %	Fraction	Limiting Concn. %
1	0.8–1.0	5	0.8–1.0	9	1.4–1.6
2	0.6–0.8	6	0.6–0.8	10	2.5–3.0
3	0.5–0.6	7	0.8–1.0	Mixture	0.8–1.0
4	0.6–0.8	8	1.2–1.4		

The lower fractions from the coal-tar dead oil show very little variation in preservative power; the high-boiling fractions are less effective than are those of lower boiling points. A certain amount of high-boiling material is, however, probably desirable in commercial creosote oil because of its effect in reducing the volatility of the oil and thus aiding in holding the oil more permanently in the wood.

A portion of coal-tar dead oil, prepared as described above, was distilled through a Hempel column, and the total distillate passing over between 190° and 310° C. was collected. To portions of this distillate, known amounts of *m*-cresol, *o*-cresol, diphenyl, naphthalene, α-methylnaphthalene, and β-methylnaphthalene were added, and the preservative efficiency of each mixture was determined. The methylnaphthalenes were purified by washing with concentrated sulfuric acid, concentrated solution of sodium hydroxide, and water, and were then steam-distilled and, finally, redistilled under reduced pressure. The other compounds were purchased as C. P. material and were not further purified. The preservative efficiencies are given in Table I.

TABLE I. PRESERVATIVE EFFICIENCIES OF COAL-TAR COMPOUNDS

Preservative	Limiting Concn. %
Dead oil (190–310° C.)	0.8–1.0
Dead oil + 1% *m*-cresol	0.8–1.0
+ 2% *m*-cresol	0.8–1.0
+ 5% *m*-cresol	0.6–0.8
+10% *m*-cresol	0.6–0.8
Dead oil + 1% *o*-cresol	0.8–1.0
+ 2% *o*-cresol	0.8–1.0
+ 5% *o*-cresol	0.6–0.8
+10% *o*-cresol	0.6–0.8
Dead oil + 1% diphenyl	0.8–1.0
+ 2% diphenyl	0.6–0.8
+ 5% diphenyl	0.6–0.8
+10% diphenyl	0.4–0.6
Dead oil + 1% naphthalene	0.8–1.0
+ 2% naphthalene	0.8–1.0
+ 5% naphthalene	0.6–0.8
+10% naphthalene	0.6–0.8
Dead oil + 1% α-methylnaphthalene	0.8–1.0
+ 2% α-methylnaphthalene	0.8–1.0
+ 5% α-methylnaphthalene	0.6–0.8
+10% α-methylnaphthalene	0.6–0.8
Dead oil + 1% β-methylnaphthalene	0.8–1.0
+ 2% β-methylnaphthalene	0.8–1.0
+ 5% β-methylnaphthalene	0.6–0.8
+10% β-methylnaphthalene	0.6–0.8
Pure *m*-cresol	0.7–0.8
Pure *o*-cresol	0.7–0.8
Pure diphenyl	0.4–0.6
Pure naphthalene	0.6–0.8
Pure α-methylnaphthalene	0.6–0.8
Pure β-methylnaphthalene	0.6–0.8

The results indicate that no one of the normal and principal components of ordinary coal-tar creosote oil is primarily responsible for the preservative action of the oil. In general, naphthalene and the methyl naphthalenes have about the same preservative efficiency as have the lower fractions of the normal dead oil, and the addition of these compounds does not increase the efficiency of the oil. Phenol and cresol are no more efficient as fungicides than are the neutral aromatic hydrocarbons, and any advantage to be derived from the presence of the tar acid in the oil must be due to causes other than the increase of the fungicidal power. Of all of the compounds studied, diphenyl alone shows more than the average preservative effect, and even this compound shows only slightly more than average efficiency.

FRACTIONS FROM WATER-GAS TAR

In view of the fact that the oils distilled from water-gas tar are used to some extent as preservative for timber, it was thought advisable to make some comparison of the preservative efficiencies of coal-tar oils and water-gas tar oils. The raw material used in the preparation of the water-gas tar oil was crude water-gas tar obtained from the Ithaca plant of the New York State Gas and Electric Corporation. The crude tar was distilled to hard pitch in an iron still, and the total distillate was collected. This distillate was then redistilled through a Hempel column, and the second distillate was collected in ten fractions of approximately equal volumes. The preservative efficiency of each fraction and of a mixture of equal parts by volume of the various fractions was then determined, using the wood pulp method. The results were as follows:

Fraction	Distn. Temp. ° C.	Limiting Concn. %	Fraction	Distn. Temp. ° C.	Limiting Concn. %
1	135–206	1.5–1.6	7	240–247	1.1–1.2
2	206–217	1.6–1.7	8	247–260	1.0–1.2
3	217–223	1.7–1.8	9	260–275	1.2–1.3
4	223–229	1.7–1.8	10	275–317	1.4–1.6
5	229–232	1.6–1.7	Mixture	....	1.7–1.8
6	232–240	1.4–1.6			

It appears that the oils from water-gas tar are only about one-half as effective as are those from coal tar. The fraction that distills between 247° and 260° C., which should contain most of the diphenyl as well as considerable amounts of naphthalene and methylnaphthalene, has definitely higher preservative power than any other fraction.

CHLORINE DERIVATIVES OF AROMATIC HYDROCARBON AND PHENOLS

It is well known that the bactericidal powers of the chlorine derivatives of the aromatic hydrocarbons and phenols are usually higher than those of the hydrocarbons or the phenols themselves. In view of this fact, it is possible that the chlorine derivatives of the components of creosote oil may be better preservatives for timber than are the compounds from which they are derived. Curtin and Bogert (*1*) measured the fungicidal powers of chlorinated naphthalene and of the crude products obtained by the direct chlorination of coal-tar creosote oil and of various crude fractions of the tar acids from creosote oil. The determinations of fungicidal power were made in standard agar-malt sirup gels, so that their results may not be directly comparable with those obtained by the wood pulp method. They concluded that: (1) The chlorination of aromatic hydrocarbons of molecular weight equal to or greater than that of naphthalene results in a decrease in toxicity; (2) the chlorination of the crude cresols or the crude xylenols from coal-tar creosote oil is accompanied by an increase in fungicidal power; and (3) chlorination of the crude mixtures of high-boiling tar acids from creosote oil, distilling between 270° and 300° C., results in a decrease in the preservative efficiency. The decrease in toxicity that was observed when high-boiling fractions were chlorinated was explained on the basis of the hypothesis that the chlorine derivatives are less soluble in water than are the hydrocarbons from which they are derived.

We have measured the preservative efficiencies of a few pure chlorine derivatives of the aromatic hydrocarbons and phenols, and the results of these tests, together with the results of tests made with the hydrocarbons and phenols themselves, were as follows:

Compound	Limiting Concn.	Compound	Limiting Concn.
	%		%
p-Dichlorobenzene	1.3–1.4	2-Chloro-5-hydroxytoluene	0.5–0.6
α-Chloronaphthalene	0.4–0.5	Phenol	0.8–1.0
β-Chloronaphthalene	0.5–0.6	*o*-Cresol	0.7–0.8
p-Chlorophenol	0.3–0.4	Naphthalene	0.6–0.8
o-Chlorophenol	0.6–0.7		

The present results agree with those of Curtin and Bogert in indicating an increase in fungicidal power upon the chlorination of the lower phenols, although the relative increase was very much less than was found by them. Contrary to their results, the writers find that the chloronaphthalenes appear to be better preservatives than is naphthalene itself, although the differences are not large. The discrepancies between our results and those of Curtin and Bogert are due, apparently, to the difference in the method used for the determination of preservative efficiencies. The former investigators used the agar plate method, in which the results depend to a marked extent upon the solubility of the preservative in water; in the wood pulp method (and probably also in service) slight variations in solubility have relatively less effect.

Literature Cited

(1) Curtin and Bogert, Ind. Eng. Chem., 19, 1231 (1927).
(2) Rhodes and Gardner, *Ibid.*, 22, 167 (1930).
(3) Schmitz and others, *Ibid.*, Anal Ed., 2, 361 (1930); see also Schmitz and Zeller, Ind. Eng. Chem., 13, 621 (1921); Schmitz and Buckman, *Ibid.*, 24, 772 (1932).

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Dry Distillation of Residue of Waste Sulfite Liquor

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IN A PAPER recently published from this laboratory (*7*) results of an investigation were presented dealing with the dry distillation of alkali lignin in a reduced atmosphere of carbon dioxide. In this paper the results are given of a similar study on the dry distillation of the residue of waste sulfite liquor.

Ahrens (*1*) was the first to make a study of the products of the dry distillation of waste sulfite liquor. He neutralized the liquor with lime, then evaporated the solution to dryness, and subjected the residue to dry distillation. The distillate was found to contain acetone and acetic acid, together with an oil containing sulfur. The carbonized residue contained 33.6 per cent ash and 4.37 per cent total sulfur.

Bantlin (*2*) partly separated the volatile sulfur compounds from waste sulfite lye by passing through it a current of air and steam. The solution was then evaporated to dryness and the residue distilled. A small yield of liquid products was obtained and no methanol, while large quantities of hydrogen sulfide and mercaptans were evolved.

In view of the rather meager information found in the literature with respect to the composition of the distillate obtained when the dry residue of waste sulfite liquor is subjected to dry distillation, the investigation described in this paper was undertaken.

Experimental Procedure

Preparation of Material. Waste sulfite liquor concentrated to the consistency of sirup was kindly furnished by The Brown Company, of Berlin, N. H. The total solids in this product amounted to 51.37 per cent.

The product was evaporated to dryness, dried at 105° C., and ground to a powder. This dry material analyzed as follows: Ash, 19.03 per cent; sulfur, 6.84 per cent; methoxyl, 6.54 per cent.

Apparatus. The apparatus described in a previous communication (*7*) was used for these experiments. The distillation experiments were carried out in a manner similar to that described in the article on the dry distillation of lignin from corncobs (*7*). For each experiment, 300 grams of the dry residue from waste sulfite liquor were used. The air in the apparatus was first replaced with dry carbon dioxide and then evacuated to 25 mm. pressure. A small stream of dry carbon dioxide at the rate of about one bubble per second was passed through the apparatus during the distillation experiment. The temperature was gradually increased until the maximum of 400° C. was obtained. The gases given off had a very obnoxious odor. The presence of hydrogen sulfide and mercaptans could be detected. The distillate consisted of a milky, aqueous liquid and an oil. Because of the relatively small amount of oil in the distillate, no attempt was made to separate it from the aqueous portion of each individual experiment. In each experiment the weight of the distillate and of the carbonized residue in the retort was determined. No attempt was made to collect the gaseous products, and the weight of the latter was obtained by difference. The results of ten experiments are given in Table I.

Table I. Products of Dry Distillation of Sulfite Lye

[300 grams material used in each experiment (222.6 grams calculated on ash- and sulfur-free basis)]

Expt.	Total Distillate (Oil + Aqueous Distillate) Weight	Yield	Yield (calcd. on ash- and S-free material)	Carbonized Residue[a] Weight	Yield	Gaseous Products[b] Weight	Yield
	Grams	%	%	*Grams*	%	*Grams*	%
1	72.0	24.0	32.3	166	55.3	62.0	20.7
2	69.0	23.0	30.9	167	55.6	64.0	21.4
3	69.0	23.0	30.9	168	56.0	63.0	21.0
4	70.0	23.3	31.4	167	55.6	63.0	21.0
5	74.5	24.8	33.4	160	53.3	65.5	21.9
6	71.0	23.6	31.8	165	55.0	64.0	21.4
7	73.5	24.5	33.0	164	54.6	62.5	20.9
8	72.0	24.0	32.3	164	54.6	64.0	21.4
9	73.0	24.3	32.7	161	53.6	66.0	22.1
10	70.0	23.3	31.4	170	56.6	60.0	20.1
Mean	71.4	23.8	32.0	165	55.0	63.6	21.2

[a] A composite sample of the carbonized residue was ashed and found to yield 35.90 per cent ash.
[b] By difference.

Examination of Aqueous Distillate

The aqueous distillates from the ten experiments were combined. To this Norit was added, the mixture was well shaken and allowed to stand at room temperature for 2 hours. This was filtered, and the filtrate made up to 1000 cc. in a volumetric flask; 250 cc. of this solution were treated with 4 per cent potassium permanganate until no further reduction took place. This was for the purpose of oxidizing volatile reducing substances, chiefly sulfurous acid. The product was made acid with sulfuric acid and distilled in a current of steam until the distillate coming over no longer reacted acid. The distillate was neutralized with sodium hydroxide and concentrated to a volume of 800 cc. Some tarry matter separated out in the course of this operation and was filtered off. The filtrate was acidified with sulfuric acid and distilled in a current of steam until all the volatile acids were driven over. The distillate was made up to a definite volume, and an aliquot titrated with 0.1 *N* sodium hydroxide solution, phenolphthalein being used as the indicator. A total of 1498.8 cc. of 0.1 *N* sodium hydroxide was used. This corresponds to 8.99 grams acid calculated as acetic acid, or 35.96 grams in total aqueous distillate (equal to 1.19 per cent yield calculated on the 3000 grams dry sulfite lye residue used, or 1.61 per cent calculated on the ash-free and sulfur-free material).

The above-mentioned solution, containing the sodium salts of volatile acids, was evaporated to dryness and a portion of the dry residue converted into the acid toluide according to the method described by Mulliken (*5*). It melted at 148.6° C. (corrected), and, when mixed with a pure specimen of aceto-*p*-toluide, no depression in the melting point was observed. The optical properties of the crystals of the toluide prepared from the sodium salt of the volatile acid obtained in the steam distillation were found to be identical with those of a known and pure specimen of aceto-*p*-toluide. The volatile acid therefore consisted chiefly of acetic acid.

Another 250-cc. sample of the aqueous distillate was made slightly alkaline with sodium hydroxide and distilled until about 150 cc. of distillate were obtained. The residual solution was acidified with phosphoric acid and distilled in a current of steam until the distillate coming over no longer reacted acid. The solution remaining in the distilling flask was filtered and exhaustively extracted with ether. The ether solution was dried over anhydrous sodium sulfate, and the ether removed by distillation. A small amount of sirup was obtained. This was subjected to distillation under reduced pressure. Nothing definite could be isolated from the small quantity of distillate obtained.

Acetone Determination. The acetone in the aqueous distillate was determined by the method of Denigès (*3*). The Messinger method (*4*) for determination of acetone could not be used because of the relatively large amounts of sulfurous acid and other sulfur compounds in the distillate. Three 25-cc. samples yielded 0.5772, 0.5677, and 0.5697 gram of precipitate, respectively. This corresponds to 0.0351, 0.0345, and 0.0347 gram acetone (mean = 0.0348 gram acetone = 1.3920 grams acetone in total aqueous distillate, or 0.046 per cent of the total weight of dry material distilled = 0.062 per cent calculated on the ash-free and sulfur-free material).

METHANOL DETERMINATION. The methanol in the aqueous distillate was determined by a method referred to in a previous communication (*6*). Two 5-cc. samples gave 0.3837 and 0.4017 gram silver iodide, and 0.0523 and 0.0547 gram methanol (= 10.70 grams—mean value—in the total aqueous distillate = 0.35 per cent calculated on the 3000 grams material distilled and 0.48 per cent calculated on the ash- and sulfur-free material.)

EXAMINATION OF OIL. The oil which had been separated from the combined distillates of all the ten experiments amounted to 46 grams (= 1.53 per cent yield calculated on the 3000 grams material distilled, or 2.0 per cent calculated on ash- and sulfur-free material). The oil was diluted with approximately three times its volume of ether, and the solution extracted with a 5 per cent solution of sodium bicarbonate. This extract was acidified with sulfuric acid and distilled in a current of steam until the distillate coming over no longer reacted acid. The total distillate was made up to a definite volume, and an aliquot was titrated with a 0.1 *N* sodium hydroxide solution; 311.7 cc. were required for the total distillate. This corresponds to 1.87 grams acid calculated as acetic (= 4.06 per cent of weight of total oil). The distillate was neutralized with sodium hydroxide and the solution evaporated to dryness. From a portion of the dry residue, the acid toluide was prepared by the method referred to above. The toluide obtained was identified as the aceto-*p*-toluide by its melting point, mixed melting point, and by the optical properties of the crystals. The volatile acid present in the sodium bicarbonate extract consisted, therefore, principally of acetic acid.

The acid liquid remaining in the distilling flask from the steam distillation mentioned above was extracted with ether, the ether solution dried over anhydrous sodium sulfate, and the ether finally removed by distillation. A small quantity of a dark brown oil was obtained. This was distilled under reduced pressure, and a very small amount of liquid came over which, on standing, partly crystallized. The amount obtained was, however, too small to permit identification.

The ethereal solution of the oil which had been extracted with a 5 per cent sodium bicarbonate solution was next exhaustively extracted with a 5 per cent sodium hydroxide solution. The alkaline extract was acidified with sulfuric acid and the solution extracted with ether. The ether solution was dried over anhydrous sodium sulfate and filtered, and the ether was distilled off. A dark brown oil was obtained. The yield was 7.5 grams (= 16.3 per cent of weight of the oil = 0.25 per cent calculated on the 3000 grams material distilled, or 0.33 per cent calculated on ash- and sulfur-free material). The oil was distilled in a current of steam. In the distillation flask there remained some tarry matter from which nothing definite could be obtained. The distillate was extracted with ether, and, after removal of the ether by distillation, an oil was obtained which amounted to 1.5 grams. Under ordinary pressure it distilled over at 200° to 210° C. The 3,5-dinitrobenzoyl derivative of this substance was prepared according to the method described in a previous communication (*8*). After three crystallizations from 95 per cent ethyl alcohol, crystals were obtained which melted at 138° C. (corrected). This agrees closely with the melting point recorded for the 3,5-dinitrobenzoylguaiacol. The optical properties of the crystals also agreed with that of 3,5-dinitrobenzoylguaiacol.

From the original mother liquor of the above, a second crop of crystals separated out. These were found to melt at 115° C. The melting point of the 3,5-dinitrobenzoyl derivative of 1-*N*-propyl-3-methoxy-4-hydroxybenzene is 116.2 ° C. (corrected) (*9*). The optical properties of the crystals agreed with those recorded for 1-*N*-propyl-3-methoxy-4-hydroxybenzene. The phenolic fraction of the oil, therefore, contained guaiacol and 1-*N*-propyl-3-methoxy-4-hydroxybenzene.

EXAMINATION OF NEUTRAL FRACTION

The ether solution of the oil which had been successively extracted with 5 per cent sodium bicarbonate solution and 5 per cent sodium hydroxide solution, was dried over anhydrous sodium sulfate and filtered, and the ether was distilled off. A dark brown oily residue was obtained which amounted to 37 grams (= 80.4 per cent of weight of oil). The oil was distilled in a current of steam, and a heavy yellow oil came over. In the distilling flask there remained a black, hard, tarry residue from which nothing definite could be obtained. The distillate was extracted with ether, the ether solution was dried over anhydrous sodium sulfate, and the ether was removed by distillation. The oily residue amounted to 26.5 grams (= 57.6 per cent calculated on the 46 grams of oil obtained from all the distillation experiments). The oil had a rather offensive odor. It was distilled under ordinary pressure and the following fractions were obtained:

Fraction ° C.	Weight Grams	Fraction ° C.	Weight Grams
150–160	2	170–180	16
160–170	2	Residue	6.5

The fraction distilling at 170° to 180° C. was redistilled, a fractionating column being used. Below 145°, 6.5 grams distilled over. The mercury column then rose rapidly, and the remainder of the oil distilled over at 170° to 172°. The weight of this fraction amounted to 6.5 grams.

The fraction which distilled over below 145° was redistilled, and it distilled over at 110° to 130°; as it was evidently a mixture, it was not analyzed.

Fraction 170° to 172° was analyzed for carbon, hydrogen, and sulfur, and the following results were obtained:

Substance, 0.1595, 0.1179, 0.1103; water, 0.0659, 0.0493, 0.0472; carbon dioxide, 0.1222, 0.0916, 0.0845.

Found: carbon 20.90, 21.18, and 20.89 per cent; hydrogen 4.62, 4.68, and 4.78 per cent.

Substance, 0.1669, 0.1452; barium sulfate, 0.8618, 0.7486.

Found: 71.15 and 71.04 per cent sulfur.

Mean: carbon 20.99; hydrogen, 4.69; sulfur, 71.09 per cent.

The identity of this fraction was not established. Presumably it was not pure.

Discussion of Results

In studying the results obtained in the distillation experiments recorded in this paper, it is of interest to compare them with those obtained in the distillation of lignin. In the following table the results of both series of experiments are presented; those obtained in the distillation of alkali lignin are taken from an article previously published from this laboratory (*7*):

	Aqueous Distillate	Oily Distillate	Caronized Residue	Gas
	%	%	%	%
Alkali lignin	11.7	28.3	50.5	9.3
Residue from waste sulfite liquor	30.0[a]	2.0[a]	55.0	21.2

[a] Calculated on the ash- and sulfur-free material.

The most striking difference between the two sets of results is the fact that the yield of oil from the residue of waste sulfite liquor is very small as compared with that obtained from alkali lignin. In the aqueous distillates, however, the relation is reversed. There is no significant difference between the yields of carbonized residue in both cases. The gas given off when alkali lignin is distilled is considerably less than that produced when the residue of waste sulfite liquor is distilled. In the latter case, the large amount of gas is attributed to a considerable extent to the hydrogen sulfide and to other volatile sulfur compounds resulting from the decomposition of the various sulfur derivatives in waste sulfite liquor. Furthermore, under the experimental conditions prevailing during the distillation, secondary reactions no doubt took place between the organic compounds and the sulfur compounds, resulting in the formation of mercaptans and products of a similar character.

The yield of acetic acid was less in the distillate from alkali lignin than that from the residue of waste sulfite liquor, whereas the yields of acetone and methanol were somewhat greater.

In the oily distillates from both materials, guaiacol and 1-*N*-propyl-3-methoxy-4-hydroxybenzene were identified. However, in the oily distillate from alkali lignin, many other compounds were definitely identified, which apparently were not present in the oily distillate from the residue of waste sulfite liquor. This may be accounted for by the fact that the chemical nature of lignin is modified considerably when it is subjected to the sulfite cooking process and also by the fact that secondary reactions take place between the sulfur derivatives and the primary degradation products of lignin.

Summary

The dry residue of waste sulfite liquor was subjected to dry distillation in a reduced atmosphere of carbon dioxide at a maximum temperature of 400° C. The following results, representing the average of ten experiments (calculated on the basis of oven-dry material) were obtained: Aqueous distillate, 22.3 per cent; oily distillate, 1.5 per cent (30.0 and 2.0 per cent, respectively, calculated on ash- and sulfur-free material); carbonized residue, 55.0 per cent; gas, 21.2 per cent (by difference).

The aqueous distillate contained acetic acid, acetone, and methanol. The yield of these three compounds (calculated on the basis of the dry material distilled) amounted to 1.19, 0.046, and 0.35 per cent, respectively. When calculated on the basis of ash- and sulfur-free material, the yields amounted to 1.61, 0.062, and 0.48 per cent, respectively.

The oil was successively extracted with 5 per cent sodium bicarbonate and 5 per cent sodium hydroxide solutions. In the sodium bicarbonate extract, acetic acid was identified. In the sodium hydroxide extract, guaiacol and 1-*N*-propyl-3-methoxy-4-hydroxybenzene were identified.

The fraction of the oil remaining after the extraction with 5 per cent sodium bicarbonate and 5 per cent sodium hydroxide solutions was steam distilled, and an oil was obtained which consisted of a mixture of sulfur-containing compounds. No definite compound was identified in this mixture.

Acknowledgment

All identifications of compounds by optical methods were made by G. L. Keenan of the Microanalytical Laboratory of the Food and Drug Administration of this department.

Literature Cited

(1) Ahrens, *Z. angew. Chem.*, **1895**, 41.
(2) Bantlin, *J. Gasbeleucht.*, **57**, 32, 55 (1914).
(3) Denigès, *Compt. rend.*, **127**, 963 (1898); *Bull. soc. chim.*, (3) **19**, 754 (1899).
(4) Messinger, *Ber.*, **21**, 3366 (1888).
(5) Mulliken, S. P., "Method for Identification of Pure Organic Compounds," Vol. I, p. 81, Wiley, 1905.
(6) Phillips, *J. Am. Chem. Soc.*, **51**, 2423 (1929).
(7) Phillips and Goss, Ind. Eng. Chem., **24**, 1436 (1932).
(8) Phillips and Keenan, *J. Am. Chem. Soc.*, **53**, 1924 (1931).
(9) *Ibid.*, **53**, 1926 (1931).

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Section of Modern Oil Cracking Unit

Dispersibility of Gas Black

I. Methods of Measuring Gas Black Dispersion

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Previous investigators have used the nature of the surface, the appearance of microsections, and various physical properties of the stock as a measure of the degree of dispersion of gas black in rubber. Here it is shown that a close relation exists between the nature of a torn surface of gas black stocks and the appearance of microsections of the stocks. The relationship is so close that the degree of dispersion which is basically shown by microsections may be measured by examining the surface. As a practical working tool standard samples of gas black stocks have been prepared and rated in percentage dispersion.

It is also shown that the character of gas black agglomerates in rubber varies from a hard, rigid type to a soft, easily dispersed variety. A microscopic study of those agglomerates aids in understanding the properties of stocks.

THE need of a method by which the degree of dispersion may be measured has long been felt by those who mix gas black into rubber. Degree of dispersion may be defined as the completeness of wetting of the pigment by the rubber or, to express it more exactly, the ratio of the pigment-rubber interface to the total available pigment surface. In this paper the dispersion of channel gas black only will be considered.

Examination of Surfaces

As mixing proceeds and more and more particles are wet by rubber, the surface appearance of the stock will gradually change from the dry, dull appearance of gas black to the glossy appearance of masticated rubber. The high surface gloss is enhanced by the intense opacity of a gas black stock and, because the reflection comes only from one plane, the surface appears almost metallic (*2*).

In the early days of the rubber industry and persisting to the present day, practical mill room men have judged the perfection of mixing by the sheen of the surface of the stock. This criterion applies particularly to gas black stocks. If the surface of the stock appears glossy and black, like a highly polished shoe, it is judged that the pigment is well dispersed. This practical method of judging the degree of dispersion is useful and reasonably accurate, although it does not tell the whole story; it has been mentioned occasionally in the literature. Wiegand (*18*) states: "In some cases, practical operatives have been able to recognize even small departures from proper dispersion by the appearance of the calendered or extruded sheet. There is, namely, a loss in smoothness and shine. This test is, however, not unambiguous and may easily lead to false conclusions."

In attempting to determine the distribution of the black inside of a piece of stock by examination of the surface, gloss is a valuable criterion, but there is another equally important factor—namely, the number and size of undispersed or almost completely undispersed lumps of black. The glossiness is a measure of the completeness with which gas black has been wet by the rubber; the undispersed chunks, large and small, are a measure of the amount of gas black which is still not at all or only slightly covered by rubber.

It is not accurate to judge dispersion in any piece of stock on the basis of either of these factors alone. For example, a piece of stock may have a high gloss but still contain many undispersed chunks of black. This indicates that part of the gas black has been thoroughly wet by the rubber but much of it has only barely started to disperse. In other instances a piece of stock may have a dull surface which close examination will show is full of small lumps of black, all of which, it may be imagined, have started to disperse. Only a small proportion of the black has been thoroughly wet by the rubber, but a large proportion has been partially wet.

Many others have recognized the importance of the undispersed or only partially dispersed chunks of gas black in judging dispersion. Wiegand (*18*) says that "even moderate departures from uniform dispersion can generally be detected with a 20-power hand magnifier on a torn surface of the mixed stock—that is, before the cure." Grenquist (*12*) studied the surface lumps and related their size and frequency to significant physical properties of the stock. He states: "The dispersion was determined by means of the microscope on freshly cut surfaces of mixtures vulcanized and unvulcanized * * *. Magnified about 300 times, the aggregates of gas black appear like a nonhomogeneous black mass, while on the smoother and more homogeneous surface of the rubber the reflection is so increased that the field remains lighted."

Grenquist cut his samples "with very sharp scissors," which in the authors' opinion does not give a surface as satisfactory as one made by tearing. Grenquist points out that the examination of the surface is a rapid method of judging dispersion and that a large surface can be studied; however, he says that "it is evident that this method is not of use in the study of the actual dispersion of the particles, but it appears to be excellent for the study of the mixing process." Grenquist characterized the dispersions as: very bad, bad, passable, good, very good, excellent.

Shepard (*15*) also discusses the surface examination of gas black stocks. He states that "the microscope is of distinct value in determining the suitability of a black for rubber reënforcement. Owing to the difficulty in preparing rubber sections for observation with transmitted light, the color tones have found little application in controlling the quality of blacks.

"Surface examination by reflected light * * * has been found of distinct value in estimating the dispersibility of a black and in evaluating various mixing procedures." Shepard shows two photomicrographs, taken by H. P. Coats, showing poor and good dispersion.

The references which have been given show that many people who have worked with gas black stocks have seen the possibility of judging dispersion by studying the character of the surface. By visual or microscopic examination they have used the surface qualities of gloss and lumps as a measure of dispersion.

Examination of Microsections

As a measure of judging the dispersion of gas black, the examination of microsections has also engaged the attention of many workers. This method is obviously limited to smaller sections and is subject to the criticism that large numbers of observations must be made if representative results are to be obtained. Pohle (*14*) has done valuable work with microsections. Depew and Ruby (*5*) show photomicrographs of sections made by freezing with carbon dioxide and cutting on a microtome which illustrate good and poor dispersion of carbon black. Hauser (*13*) mentions that in microsections made as described by Dannenberg (*4*) the degree of dispersion may be measured either by counting the aggregates or in some cases by colorimetric methods.

Green (*7*), in a paper on the stretching of rubber stocks, gave some photomicrographs which showed the stretching of agglomerates that were presumably of carbon black. In a paper (*8*) on a method of making microsections he showed photomicrographs of undispersed carbon black.

In another paper (*9*) Green stated, as a result of examining microsections, that "all gas black contains large lumps of undispersible material which are probably adamantine," and that "poor incorporation of gas black will show as dense, black lumps."

Spear and Moore (*16*) also describe a method of making microsections and show photomicrographs of some carbon black stocks, but in their published pictures the agglomerates are rather obscure. Grenquist (*10*) showed some photomicrographs and discussed the dispersion of gas black in rubber, but he worked only with stocks containing a low concentration of black. In another paper (*11*) Grenquist describes microsections made of stretched stock by freezing and cutting on a microtome, and he showed the formation of vacuoles chiefly around aggregates of black or other pigments.

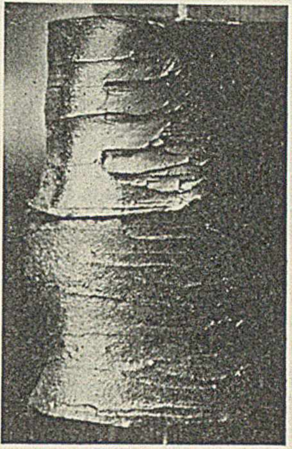
FIGURE 1. TORN SECTIONS OF TWO GAS BLACK STOCKS (× 2)

PHYSICAL PROPERTIES INDICATIVE OF DISPERSION

Aside from microscopic methods, certain physical properties have been recommended to indicate the degree of dispersion. Wiegand (*18*) states: "I think the most sensitive index (for good dispersion) is tensile strength. Within the past year I have had personally an opportunity of observing several cases where improved dispersion notably increased the tensile, in some cases up to 25 per cent." Grenquist (*12*) also related dispersion to tensile. Wiegand further stated that "another way is through irregularity in breaks. Although not a refined or quantitative means of measuring bad dispersion, it is nevertheless an excellent qualitative warning." Endres (*6*) discussed the effect of agglomeration on physical properties and showed some photomicrographs of special carbon blacks.

Inspired by a paper of Stamberger (*17*) on the rate of diffusion and settling of different pigments, Carson and Sebrell (*3*) centrifuged rubber cements containing different carbon blacks and found a relation between the amount of black left in suspension and the modulus at 500 per cent. While their method required perfect dispersion of the blacks and was indicative only of particle size or of specific surface, it could conceivably be used as a measure of dispersion in which undispersed agglomerates act as large particles.

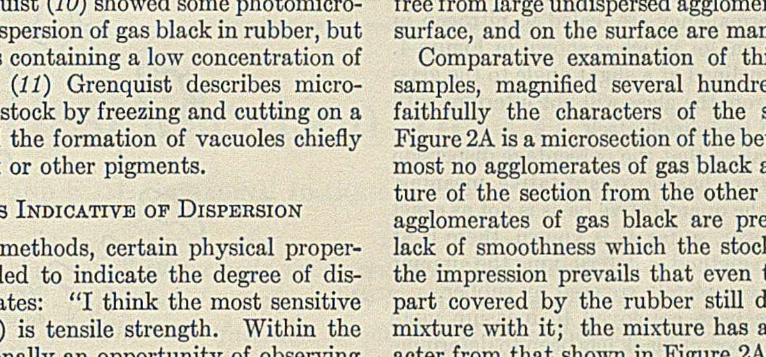
FIGURE 2. MICROSECTION OF THE TWO STOCKS OF FIGURE 1 (× 200)

A. Better dispersed stock B. Stock showing gas black agglomerates

Shepard (*15*) points out that flex-cracking is related to dispersion. This property is obviously most valuable as an indication of poor dispersion.

It may be concluded that many physical properties are related to the degree of dispersion, and the proof of such a relationship would be of scientific and practical interest. Irrespective of the objectives sought by those who have previously suggested physical properties as a measure of dispersion, no one is interested in measuring dispersion by first measuring some physical property, but everyone is interested in first measuring the degree of dispersion and from that concluding that the tensile, tear resistance, flex cracking, or tread wear will be satisfactory, if other factors are constant.

RELATION BETWEEN MICROSCOPIC AND MACROSCOPIC APPEARANCE OF GAS BLACK STOCKS

If small pieces are torn from two gas black stocks and these torn surfaces are examined with the naked eye or under a low-power microscope, a difference may be found in their appearance. Two such stocks, so selected that there is a difference, are shown in Figure 1. One of these is extremely glossy and relatively free from large undispersed agglomerates; the other has a dull surface, and on the surface are many undispersed lumps.

Comparative examination of thin sections of these two samples, magnified several hundred times, illustrates how faithfully the characters of the stocks are again shown. Figure 2A is a microsection of the better dispersed stock. Almost no agglomerates of gas black are observed. In the picture of the section from the other stock (Figure 2B), many agglomerates of gas black are present. From the general lack of smoothness which the stock of Figure 2B possesses, the impression prevails that even the gas black which is in part covered by the rubber still does not form a coherent mixture with it; the mixture has an entirely different character from that shown in Figure 2A. This impression is further heightened by the appearance of the edges of the two sections. In Figure 2A the edges are smooth, straight, and coherent; in 2B the edges of the section are jagged, irregular, and give the impression that the stock is noncoherent. If the torn surfaces of other samples of stock are compared with microsections made from them, close relationship between the surface appearance and the appearance of microsections will be found in each case.

These sections were made by the method developed by one of the authors (*1*). This method is used because it is rapid and effective but more particularly because by its use the coherent character of the stock and the nature of the agglomerates can be better shown than by methods which employ a microtome.

ESTABLISHMENT OF A QUANTITATIVE STANDARD

The information gained by the microscopic examination of thin sections or by the examination of the surface of a piece of stock is subjective and not strictly quantitative. However, in practice and in the actual study of mixing procedures, the appearance of either torn surfaces or microsections is a dependable method in the hands of an experienced observer. In order to make the method of still more service, it was found desirable to express the surface appearance in terms of actual numbers. For example, the better dispersed sample of Figure 1 was rated 90 per cent, the poorer, 70 per cent. Although it was found possible for one observer, examining many samples each day, to duplicate and check his judgment, the need for a set of standard samples in the interest of accuracy was apparent. The standards which were prepared are mixtures of rubber and gas black only (65:35), prepared by mixing for different times in the improved Schiller mixer (Figure 3). The samples themselves are torn from the resulting stocks and for permanency are sealed in nitrogen in small, hard-rubber boxes, one of which is shown in Figure 4. The face of the sample is inclined at a slight angle to the glass top so that the reflection from the glass will not interfere with the surface appearance of the sample itself.

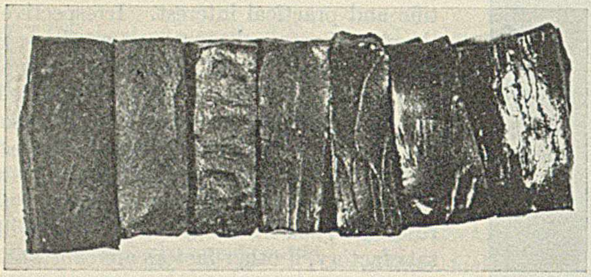

Figure 3. Standard Samples of Gas Black Stocks

The objection may be raised that the percentage dispersion expressed by these numbers has no quantitative meaning. It is freely admitted that the quantitative basis is not as exact as one could wish. However, so far as is known, there is at present no rigidly accurate method of determining the amount of channel black which is completely covered by rubber.

One method which has been employed to measure more exactly the degree of dispersion of black has been to determine the ratio of areas covered by opaque agglomerates to the total area under observation. This ratio has been determined for these standard samples, but the prepared set does not follow these measurements exactly. For example, a drawing showing the outlines of the opaque agglomerates in a microsection made from the 65 per cent sample is shown in Figure 5. The agglomerates in this particular area are approximately 29 per cent of the total area, instead of the 35 per cent which they should be if this ratio were the basis of the standards.

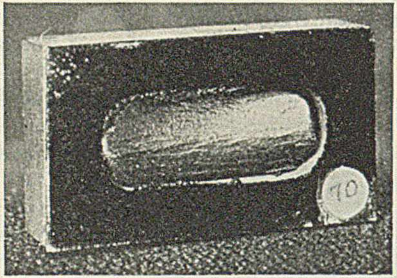

Figure 4. Hard-Rubber Box for Storing Gas Black Sample

Further consideration of the opaque areas to the total area is not warranted for two reasons: (1) The exact composition of the opaque areas is not known, although, from careful observation of sections of varying thickness, it would be concluded that the opaque areas contain from 50 to 90 per cent of channel black and from 50 to 10 per cent of rubber. (2) If the ratio of areas is used as a basis for quantitative measurement, the importance of surface gloss is not sufficiently emphasized.

When using these standards it has been found that different observers can check each other with accuracy. Certain precautions are necessary in preparing the samples of stock which are to be compared with the standards:

1. The sample should be torn by gripping firmly on each side of a slit cut in the stock and pulling with as little stretching as possible. This procedure is recommended because in the writers' experience the character of the stock is shown better by a torn surface than by a cut surface. A cutting tool smears rubber over the surface of gas black lumps and, furthermore, makes a poor piece of rubber stock appear more coherent than tearing reveals it to be.
2. The stock from which the sample is torn must not be warm.
3. The sheet should preferably be 6 to 8 mm. thick.
4. Uniform procedure should be followed in taking samples from the rubber mill; for example, the samples should always be taken from the mills at the same stage of the mixing operation.

The use of these standard samples as a means of giving a quantitative value to the degree of dispersion of stocks has proved useful in studying factory operations. In the next paper of this series some of its uses in the study of experimental mixing will be discussed.

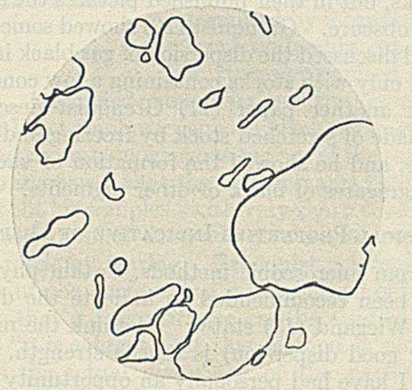

Figure 5. Outlines of Opaque Agglomerates in 65 Per Cent Sample (× 100)

Types of Agglomerates in Channel Gas Black

It may safely be said that the appearance of a torn surface of a gas black stock gives an accurate picture of the degree to which the gas black is dispersed; a surface which is full of undispersed lumps of black unmistakably indicates that thin sections also will show the presence of undispersed agglomerates. However, the surface appearance will tell little or nothing about the nature of the agglomerates.

In general, there are two types of gas black agglomerates. From their behavior during the mixing process they may be described by the simple terms "soft" and "hard." In Figure 6A are several typical soft agglomerates. They give the appearance of being in the process of dispersing. The edges are not sharp or rigid, and the separate particles in the agglomerate are partially covered by rubber. In strong contrast to these soft, easily dispersing agglomerates, the hard agglomerates have sharp, rigid edges. A picture of one is shown in Figure 6B. From the sharp edges and from the fact that the particle has actually broken away from the rubber, one would conclude that they have only slight compatability with rubber and that large forces will be necessary to break them up and cause their separate particles to be covered

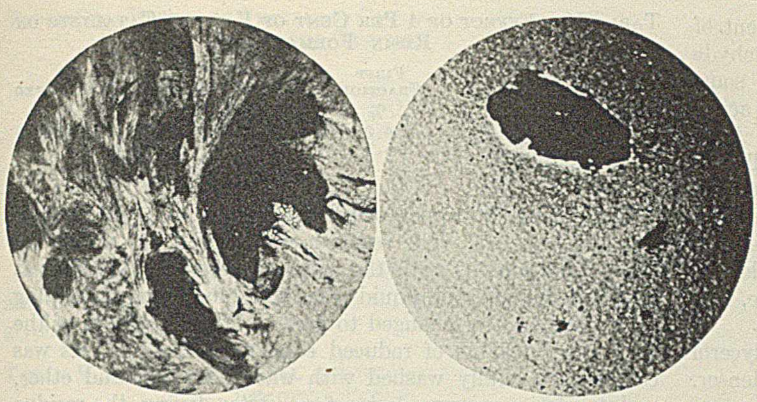

FIGURE 6. MICROSECTIONS OF AGGLOMERATES (× 200)

A. Soft agglomerates B. Hard agglomerates

by rubber. As a matter of fact, most of these particles are eventually dispersed by high shearing forces on further milling, although a small percentage of them are so hard that, if broken, they shatter only into rather large particles 1 to 10 microns in diameter. These hard particles are probably the true grit which is present to some extent in most channel blacks.

All channel blacks contain some of both types of agglomerates; those which disperse easily contain only a small percentage of the hard variety, while the less easily dispersing blacks contain a somewhat larger percentage of this type. The presence of the two types must be taken into consideration in any discussion of the mixing process because of their effect upon the character of rubber compounds, cured and uncured.

LITERATURE CITED

(1) Allen, IND. ENG. CHEM., Anal. Ed., **2**, 311 (1930).
(2) Bancroft and Allen, *J. Phys. Chem.*, **29**, 565 (1925).
(3) Carson and Sebrell, IND. ENG. CHEM., **21**, 914 (1929).
(4) Dannenberg, *Kautschuk*, **1926**, 276.
(5) Depew and Ruby, J. IND. ENG. CHEM., **12**, 1156 (1920).
(6) Endres, *Ibid.*, **16**, 1148 (1924).
(7) Green, *Ibid.*, **13**, 1029 (1921).
(8) *Ibid.*, **13**, 1130 (1921).
(9) Green, *Chem. & Met. Eng.*, **28**, 53 (1923).
(10) Grenquist, IND. ENG. CHEM., **20**, 1074 (1928).
(11) Grenquist, *Ibid.*, **21**, 665 (1929).
(12) Grenquist, *Rev. gén. caoutchouc*, **7**, No. 63, 17 (1930); *Rubber Chem. Tech.*, **4**, 29 (1931).
(13) Hauser, "Colloid Chemistry of the Rubber Industry," p. 38, Oxford Univ. Press, London, 1928.
(14) Pohle, *Kolloid-Z.*, **38**, 75; **39**, 1 (1926); *Z. wiss. Mikroskop.*, **44**, 183 (1927); *Gummi-Ztg.*, **42**, 2687 (1928).
(15) Shepard (in Alexander's "Colloid Chemistry"), Vol. IV, p. 342, Chemical Catalog, 1926.
(16) Spear and Moore, IND. ENG. CHEM., **17**, 936 (1925).
(17) Stamberger, *Kolloid-Z.*, **42**, 295 (1927).
(18) Wiegand, *India Rubber J.*, **73**, 33 (1927).

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Resinification of Glycerol

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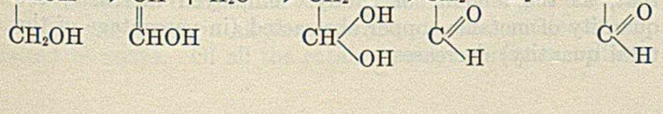
New methods are described to obtain resin-like products from glycerol by heating with a catalyst. The most favorable conditions of resinification have been determined experimentally. Good catalysts for the reaction are found to be easily reduced salts of sulfurous and of sulfuric acids, and also these acids themselves. The best catalysts are mercurous and copper sulfates.

A description of the properties of the glycerol resin obtained and data on its chemical composition are given.

THE preparation of aldehyde resins (especially acetaldehyde, crotonaldehyde, acrolein) has been known for a long time and been the subject of many researches. When obtaining aldehyde resins by condensation, it is usual to apply alkalies and alkaline agents as catalysts. When the catalysts are not present, pressure should be applied.

Among the aldehydes suitable for industrial purposes is acrolein, which is obtained by heating glycerol in the presence of dehydrating reagents, such as sulfuric acid, potassium sulfate, etc. At first, water separates from the glycerol, yielding an unsaturated alcohol containing hydroxyl at the double bond (step I of the following reaction). The alcohol immediately recombines with water (step II) forming an unstable compound which dehydrates, yielding an aldehyde alcohol (step III). The latter on further dehydration is transformed into an aldedyde—acrolein:



When stored, acrolein easily becomes an amorphous white substance, disacryl, which is insoluble in water, alcohol, acids, and alkalies. Satisfactory methods for the preparation of acrolein have been described by Wohl and Mylo (*5*), Witzemann (*4*), Moureu (*2*). During the war Moureu, Boutaric, and Dufraisse (*3*) worked out a method of obtaining cheap acrolein and of completely stabilizing it. Stabilized acrolein can be stored and serves as a raw material for special resins known in industry as Orka.

Pure acrolein polymerizes in the cold in the presence of inorganic and organic bases. After washing and desiccating, the polymerized product is a white powder melting between 80° and 100° C. It is insoluble in water and in hydrocarbons, but is soluble in most other organic solvents and is a suitable substance for the preparation of varnishes.

Acrolein also condenses with phenols in the presence of catalysts, yielding a hard resin. Such resins have been proposed as suitable insulating materials for electrotechnical purposes.

McLeod (*1*) shows that all alkalies, weak as well as strong, convert acrolein, in cold water solutions, quantitatively to a polymeric form. To effect this, only traces of alkalies are necessary, and during this process heat is evolved.

Present experiments were based on a direct treatment of glycerol to obtain resinous-like products of the aldehyde type. It was found that by heating glycerol with some sulfate or sulfite, as well as with sulfuric or sulfurous acids, glycerol formed resins in considerable quantities. After heating glycerol with mercurous sulfate as catalyst, followed by desiccation in a vacuum, a dark colored viscous resin is formed which is soluble in water, in alcohol, and in a mixture of alcohol with benzene, and partly soluble in acetone. When heated as a thin layer, the resin forms a glossy flexible film, which is insoluble in water, alcohol, and acetone, and is also unaffected by weak acids and alkalies.

Such resin-like products are obtained by heating glycerol several hours in a round-bottom flask under reflux condenser. Soon after the heating starts, the reacting mixture changes its color to a milky white, then grayish, and finally vivid yellow color. Simultaneously small drops of reduced metallic mercury are precipitated at the bottom of the flask. The boiling point of the mixture falls from 170° to 145° C. because of the liberation of the water formed during the reaction. A dark brown liquid is obtained with a peculiar odor which resembles somewhat that of burned sugar; it is thicker than glycerol. The liquid distilled under vacuum gives two fractions: one at 35° to 55° C. and a pressure of 25 mm., and the other 120° to 145° C. and a pressure of 25 mm. The residue is a resin whose weight represents 65 to 70 per cent of the weight of the glycerol used. The first fraction is a transparent colorless liquid possessing a rather sharp odor; the second is a transparent yellow liquid with an extremely sharp odor which irritates the mucous membranes. Both fractions give reactions characteristic of aldehydes: They reduce Fehling solution, react with ammoniacal silver nitrate solution, discolor bromine water, etc.

The present experiments were carried out with pure glycerol having the following properties: density at 15° C., 1.252; glycerol content (by acetone method), 95.42 per cent; refractive index, 1.4651 at 28° C.

Table I shows the results of the experiments to determine the influence of amount of catalyst (mercurous sulfate) on the quantity of resin formed after treatment for 12 hours.

TABLE I. EFFECT OF VARYING AMOUNTS OF MERCUROUS SULFATE ON RESIN OBTAINED[a]

Expt.	Catalyst Used	Resin Obtained	Liquid Products of Distn.
	%	*Per cent by weight of glycerol*	
1	4	61.9	35.9
2	2	58.7	30.7
3	0.5	45.8	40.4

[a] The losses during reaction take place at the expense of the noncondensed products.

Thus, glycerol, treated with mercurous sulfate, forms 46 to 62 per cent of resin when treated with 0.5 to 4 per cent of the catalyst.

Other mercury salts were also employed, such as mercurous nitrate, mercurous chloride, and mercuric chloride. The glycerol was treated as before. The reaction lasted 12 hours; 4 per cent of catalyst was added in each case. When condensed, the product was brown at the end of the reaction. At the bottom of the retort drops of metallic mercury were precipitated. This was weighed to determine the quantity of reduced mercury. The condensed product was distilled under vacuum. Water distilled over first at 29° to 45° C. and a pressure of 23 to 25 mm., then glycerol at 179° to 183° and a pressure of 22 mm. An insignificant quantity of resin-like, dark residue was left. Results are given in Table II.

With these catalysts, glycerol gave only insignificant amounts of resin. This indicates the importance of the acid residue of the salt employed as catalyst.

TABLE II. EFFECT OF 4 PER CENT OF VARIOUS CATALYSTS ON RESIN FORMATION

Expt.	Catalyst	First Fraction	Glycerol	Residue	Hg Abstracted
		%	%	%	%
1	$HgNO_3 \cdot H_2O$	6.3	87.7	2.3	94.98
2	$HgCl$	5.7	82.7	7.4	...
3	$HgCl_2$	7.6	75.7	10.7	...

The action of copper sulfate ($CuSO_4.5H_2O$) on glycerol was studied next. The reaction was carried out under the same conditions as with the salts of mercury. When heat was first applied, the liquid was light blue; but as heating went on, the color changed to green. At the bottom of the flask a red residue of reduced copper appeared. This was collected, carefully washed with water, alcohol, and ether, and dried in a vacuum desiccator. After drying, the residue was a fine, rosy red powder; it was insoluble in ammonia and in strong sulfuric acid but dissolved quickly in nitric acid. When ground in a small agate mortar, the residue gave a metallic glitter. Under a microscope glittering metallic fragments were seen. An analysis was made of this residue according to Schiloff's iodometric method, based on the reaction,

$$2Cu + 4I = 2CuI + I_2$$

showed 98.9 per cent copper content. After filtering, the condensed product was dried under vacuum at 20 to 25 mm. Two fractions were distilled: the first at 35° to 56° C., the second at 120° to 140° C.

The resin residue was 60 per cent by weight of the glycerol employed. Both fractions gave reactions showing aldehyde content. The resin has properties analogous to those of the resin obtained by condensation of glycerol with mercurous sulfate.

TABLE III. EFFECT OF LENGTH OF REACTION PERIOD ON QUANTITY OF RESIN

(Catalyst used, 4 per cent copper sulfate)

Expt.	Condensation Period	Losses during Condensation	Resin Obtained	Liquid Product of Distn.	Total Balance	Copper Abstracted
	Hours	%	%	%	%	%
1	6	...	16.2	72.5	..	..
2	8	...	61.5	34.5	96.0	..
3	10	0.2	66.4	31.4	98.0	67.2
4	12	1.0	66.5	41.2	98.7	..
5	14	0.1	69.8	28.1	98.0	68.8
6	16	...	62.1	36.6	98.7	..
7	18	...	66.3	31.7	98.0	..
8	20	2.5	65.2	31.5	99.2	68.4
9	30	1.0	65.4	33.1	99.5	68.2

EFFECT OF CONDENSATION PERIOD ON QUANTITY OF RESIN OBTAINED

The condensation was carried on in an analogous manner under reflux condenser and with subsequent dehydration under vacuum. Four per cent catalyst was used in all the experiments. The condensation period varied from 6 to 30 hours. Most resin was formed during the 14-hour reaction period. The mean quantity of resin obtained was 68.25 per cent.

EFFECT OF AMOUNT OF CATALYST ON QUANTITY OF RESIN OBTAINED

The glycerol was treated again under reflux condenser with subsequent dehydration under vacuum. The condensation period was 14 hours for all experiments, the quantity of catalyst varied from 1 to 6 per cent. Results are shown in Table IV.

The experiments show that the maximum quantity of resin is obtained when using 4 per cent of catalyst, and that, as the amount of catalyst employed increases, the quantity of metallic copper abstracted (in percentage of the total quantity) decreases.

Table IV. Effect of Amount of Catalyst Used on Quantity of Resin Obtained

Expt.	Catalyst	Loss in Weight during Condensation	Resin Obtained	Liquid Product of Distn.	Total Balance	Copper Ppt. Abstracted
	%	%	%	%	%	%
1	1	0.6	62.3	28.2	91.1	75.5
2	2	0.4	62.0	30.0	92.4	74.0
3	4	1.5	68.3	26.9	96.7	68.8
4	6	0.8	65.3	28.4	94.5	62.6

Other experiments were made with 2 per cent of catalyst and a condensation period of 30 to 36 hours. Results are given in Table V.

Table V. Effect of Small Amount of Catalyst and Long Reaction Period

Expt.	Condensation Period	Loss in Weight	Quantity of Resin Obtained	Liquid Products of Distn.	Total Balance
	Hours	%	%	%	%
1	30	0.2	65.4	34.2	99.7
2	32	0.7	65.4	29.3	95.4
3	34	1.0	65.8	28.9	95.7
4	36	2.0	66.3	26.7	95.0

On the average the quantity of resin did not vary under these conditions.

In order to determine more completely the composition of the liquid obtained during the treatment of glycerol, the liquid product was treated by heating under reflux condenser with one per cent of potassium carbonate at 95° to 105° C. during 4 and 8 hours, respectively. After the end of the process a viscous yellow resin was formed on the bottom of the flask. The aqueous layer was a turbid liquid with a faint odor of acrolein; it gave the aldehyde reaction with silver nitrate. After being washed and dried, the resin was ignited (according to Liebig's method), and its composition determined. It was found to be similar to that of the acrolein resin (Orka) generally obtained from pure acrolein:

	C	H	O (by Difference)
	%	%	%
Resin obtained from product of distn.	54.91	7.81	37.28
	54.77	7.84	37.39
Resin (Orka) obtained from pure acrolein	54.82	7.63	37.55
	54.54	7.65	37.81

The solubility of both products is identical. This investigation of the resinous-like product obtained from the liquid product of distillation confirms the presence of acrolein.

In order to determine the aldehyde content the product of distillation was oxidized (using hydrogen peroxide), after first determining by titration the quantities of acids obtained by oxidation. The results obtained were calculated as acrolein. The acrolein content in the distillate varied from 12 to 15 per cent.

Thus, the quantity of resin obtained does not vary whether the glycerol is treated to give an aqueous acrolein fraction which is distilled off or whether it is treated under reflux condenser.

Effect of Other Sulfates on Glycerol

Sulfates of different metals were chosen as catalysts: aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$; cobaltous sulfate, $CoSO_4 \cdot 7H_2O$; ferrous sulfate, $FeSO_4 \cdot 7H_2O$; calcium sulfate, $CaSO_4 \cdot 2H_2O$; sodium sulfate, $Na_2SO_4 \cdot 10H_2O$; zinc sulfate, $ZnSO_4 \cdot 7H_2O$; manganese sulfate, $MnSO_4 \cdot 7H_2O$; cadmium sulfate, $3CdSO_4 \cdot 8H_2O$; nickel sulfate, $NiSO_4 \cdot 7H_2O$; titanium sulfate $Ti(SO_4)_2 \cdot 7H_2O$; magnesium sulfate, $MgSO_4 \cdot 7H_2O$; and lithium sulfate, Li_2SO_4.

The reaction was carried on under reflux condenser and by subsequent desiccation under vacuum; 4 per cent of catalyst was used in all the experiments, and condensation lasted 14 hours. Of all the catalysts only aluminum sulfate and titanium sulfate gave a perceptible resin formation. In all other cases, glycerol was distilled.

Table VI. Effect of Aluminum and Titanium Sulfates on Glycerol

Expt.	Catalyst	Loss in Weight during Condensation	Resin Obtained	Liquid Product of Distn.	Ash in Resin	Acid Coefficient of Resin 1	Acid Coefficient of Resin 2	Mean Aldehyde Value First fraction	Mean Aldehyde Value Second fraction
		%	%	%	%				
1	$Al_2(SO_4)_3 \cdot 18H_2O$	0.6	55.4	43.1	1.46	32	31	0.6	17.2
2	$Al_2(SO_4)_3 \cdot 18H_2O$	0.7	54.5	39.1	0.97	..	..	...	..
3	$Ti(SO_4)_2 \cdot 7H_2O$	0.3	49.7	33.3	0.15	26	27	1.3	5.3
4	$TiSO_4 \cdot 7H_2O$	0.3	49.0	26.6	..	..	..	...	..

The considerable loss sustained during the condensation of glycerol with titanium sulfate is caused by the difficulty of filtering the condensed product (to separate the catalyst).

The quality of resin obtained when condensing glycerol with aluminum or titanium sulfates is inferior to that obtained in the presence of copper and mercury sulfates. These experiments show that salts which are easily reduced to metals (as copper or mercury) contribute to the formation of resin; with other salts, either no resin or only small quantities are formed.

When glycerol is treated under similar conditions by 4 per cent of sodium sulfate and subsequently dried under vacuum, a liquid fraction is obtained (8.9 per cent at 44° to 45° C. and a pressure of 40 mm.). During the distillation the reaction mass is turbulent and foams; this impedes the operation. The resinous-like residue has a sharp, disagreeable odor; when mixed with water it makes it turbid.

In order to confirm the conclusion (drawn from the above experiments) concerning the predominant part played by sulfuric acid in the formation of resin, glycerol was condensed with sulfuric acid as follows: Two experiments were carried out treating glycerol under reflux condenser with subsequent desiccation under vacuum, and two operations with simultaneous separation of the aqueous acrolein fraction formed during the reaction. The resin was soluble in water, alcohol, in a mixture of alcohol and benzene, and also partly in acetone.

Table VII. Effect of 0.5 Per Cent Sulfuric Acid on Resin Formation

Expt.	Method of Condensation	Condensation Period	Loss of Wt.	Resin Obtained	Liquid Product of Distn.	Acid Coefficient 1	Acid Coefficient 2	Aldehyde Value First fraction	Aldehyde Value Second fraction
		Hours	%	%	%				
1	Under reflux condenser	14	1.1	64.7	32.0	10.2	11	1.8	6.8
2	Same as 1	14	1.2	66.6	33.1	10	10	..	..
3	With distn. of aqueous acrolein fraction	5	...	66.6	33.3	31	32	13.2	13.2
4	Same as 3	5	...	66.3	33.7	..	..	14.4	14.4

Effect of Sulfur Dioxide on Glycerol

The sulfur dioxide was passed through the heated glycerol for 6 hours at the boiling temperature of the mass (170° to 210° C.). The reacting mass became gradually darker until a dark brown color was reached. When separated under vacuum, two fractions appeared: the first at 48° to 65° C. and a pressure of 80 mm.; the second at 140° to 160° C. and a pressure of 80 mm. The residue in the flask was about 48 per cent resin:

Expt.	First Fraction	Second Fraction	Resin
	%	%	%
1	2.3	37.2	47.9
2	3.1	38.5	48.2

When using sulfur dioxide mixed with air in the ratio of 1 to 3 by volume, treating the glycerol under similar conditions, the quantities of resin obtained were 37.5 and 39.8 per cent, respectively. If glycerol is previously treated by sulfur dioxide at room temperature, and heated further under reflux condenser, resin is not formed in appreciable quantities.

Effect of Copper Sulfite

Using 2 per cent copper sulfite as catalyst, glycerol was again treated in the usual manner by heating (under reflux condenser for 4 hours) up to the boiling point of the reacting mass (137° to 154° C.), and by separating subsequently under vacuum.

Table VIII. Effect of Copper Sulfite on Resin Formation

Expt.	Loss in Weight during Condensation	Resin Obtained	Liquid Product of Distn.	Ash in Resin	Aldehyde Value of Liquid Product 1	2
	%	%	%	%		
1	1.3	52.6	41.1	0.19	14.03	14.11
2	0.5	52.1	42.3	..	...	...

In order to test the catalytic effect of metals, copper and mercury were tried; their catalytic action is best as sulfates. When glycerol was treated in the usual manner in the presence of small pieces of mercury or of copper, no resin formation was observed. When dried under vacuum, almost pure glycerol was separated.

In order to study the effect of other mineral acids, glycerol was treated with hydrochloric and nitric acids. The reaction was carried on under reflux condenser and with subsequent desiccation under vacuum. No resinification of the glycerol took place.

Composition of Resin

Having established the optima conditions for the formation of resin, the composition of the resin and of the product separated were studied; at the same time, attempts were made to improve the quality of the resin by increasing its hardness in the nonpolymerized state.

An attempt was made thoroughly to combine all the aldehyde. After carrying out the usual reaction for 14 hours, phenol was added (in the ratio of one molecule of phenol to one of acrolein); heating was continued for 3 and 2 hours, respectively, with subsequent desiccation under vacuum. The following phenomena were noticed: If the reaction takes place at the boiling temperature of the mixture (153° to 158° C.) then, during the vacuum-drying, about 7 per cent of water with phenol is separated out first (at 34° to 55° C. and a pressure of 17 to 18 mm.); no acrolein odor is noticed in the product separated. As residue, a powder-like, brick-red mass is left which is insoluble in water, benzene, and 10 per cent sulfuric acid, but is partly soluble in alcohol and 10 per cent alkali.

But, if the temperature of the reaction is held within 85° to 90° C., during the desiccation under vacuum, water and phenol are separated out at first (at 35° to 80° C. and a pressure of 20 mm.) and then resin is formed as usual. The quantity of resin obtained was 63.5 per cent, and of the separated aldehyde, 21.45 per cent.

When using ammonia as catalyst (3 per cent of the weight of phenol), analogous results are obtained. After a 14-hour reaction phenol and ammonia were added, and the operation was continued for 2 hours at 90° C. When desiccating under vacuum, first water with phenol was separated out, and then the water-acrolein fraction with formation of resin. The amounts obtained were as follows:

Expt.	Resin	Separated Aldehyde
	%	%
1	56.5	26.9
2	58.3	30.2

Thus, by adding phenol during the reaction and by further heating the mixture at boiling temperature, aldehyde combines with phenol, forming a powder-like mass which consists of 85 to 90 per cent of the weight of the glycerol employed. On the other hand, if the temperature of the reaction is held at 90° C., then the phenol which did not take part in the reaction is separated, and in addition the usual formation of resin and of a water-acrolein fraction takes place.

Another attempt to combine the aldehyde contained in the separated product consisted in treating the reacting mass with alkali for the purpose of polymerizing the acrolein. Glycerol was treated with 4 per cent $CuSO_4 \cdot 5H_2O$, and, after heating 14 hours, enough sodium hydroxide was added to obtain a 5 per cent solution; then heating was continued for 3, 2, and 1 hour, respectively, at the boiling temperature of the mixture (134° to 138° C.). In all cases glycerol was regenerated during the vacuum desiccation.

Table IX. Vacuum Separation

Expt.	Condensation Period	First Fraction	Glycerol	Residue
	Hours	%	%	%
1	3	4.5	79.3	7.75
2	2	5.2	77.8	7.15
3	1	4.2	82.2	5.35

The first fraction was a colorless, transparent liquid with a slight acrolein odor. It separated at 55° to 80° C. and a pressure of 14 to 15 mm. The second fraction was glycerol which separated at 178° to 185° C. and the same pressure. The residue was a powder-like, brick-red mass. The regeneration of glycerol can be explained thus: Acrolein is formed from glycerol, it seems, only when the water is separated out, but, on the other hand, the addition of alkali neutralizes the catalyst before the separation of the water. To verify this, a vacuum separation of the glycerol was made with 4 per cent $CaSO_4 \cdot 5H_2O$ without previous condensation under reflux condenser.

Table X. Results of Vacuum Separation

Fraction	Temp.	Pressure	Resin Obtained
	° *C.*	*Mm.*	%
1	45– 55	30	6.38
2	180–183	25	44.00
3	120– 90	32	2.58
Resin	.....	..	46.95
			99.91

Thus a considerable amount of resin was formed by direct vacuum distillation of glycerol with the catalyst.

Treatment of Glycol. Ethylene glycol was treated with 2 and 4 per cent of mercurous sulfate and 2 and 4 per cent of copper sulfate under reflux condenser, followed by vacuum separation. In none of the cases was formation of resin observed.

Properties of Resin. The typical resin obtained from glycerol—e. g., when treated with mercurous or copper sulfate—is a viscous, dark brown mass soluble in water, alcohol, acetone, and a mixture of alcohol with benzene. When heated, the resin becomes nonfusible and is capable of forming flexible films. When polymerized to a nonfusible and insoluble state, the resin loses from 10 to 15 per cent of its weight. If the resin has been dissolved in water and the solution distilled with steam, a part of the resin is abstracted in a hard state. The precipitated resin is insoluble in water (cold or hot), is brittle, and shines when broken. It is soluble in alcohol and in alkaline water. The quantity of resin precipitated from the aqueous solution varies within wide limits from 31 to 59 per cent (data of sixteen experiments). The greater the viscosity of the primary raw material, the greater is the quantity of hard resin obtained.

There is no glycerol in the liquid separated out, but traces of aldehydes are to be found. If the resin is isolated from the solution by filtering and if the solution is evaporated (in a water bath), as residuum a viscous, colored liquid soluble in water is obtained. Further separation with steam of the filtrate when a certain limit of precipitation has been attained (within 31 to 59 per cent of the weight of the original resin) does not give any more precipitated resin. But if the residue obtained after the evaporation of the filtrate is treated with a catalyst (e. g., copper sulfate) and then separated under vacuum, after the residue has been dissolved in water and distilled with steam, the precipitation of hard resin is again observed. Thus, in one experiment, starting with 245 grams of resin, there was obtained after the first separation of the solution of resin in water (with the aid of steam) 91.8 grams of hard resin (37.4 per cent); then, after evaporating the filtrate, treating the residue with 4 per cent $CuSO_4 \cdot 5H_2O$, and separating it under vacuum, there were obtained 155.4 grams of resin (the liquid part separated contains 2.9 per cent of aldehyde, considered acrolein). When separating (with the aid of steam) the aqueous solution of this "secondary" resin, hard resin was again abstracted which was 15.5 per cent of the weight of the original glycerol used for the reaction. If the same operation is repeated with the secondary filtrate, a certain quantity of "tertiary" resin is obtained, and so on. The precipitated resin is dark brown, and its temperature of fusibility is between 50° and 70° C.

The amount of ash in the precipitated resin is about 0.08 per cent. The resin does not contain combined sulfur (determined by fusing with metallic sodium, dissolving, and testing for a color reaction with sodium nitroprusside and sulfuric acid); it has the properties of aldehydes (reduces Fehling solution, reacts with ammoniacal solution of silver nitrate). The resin gives a weak acid reaction and is soluble in alkali. An elementary analysis of the resin (according to Liebig) gave the following results:

C	H	O
%	%	%
60.76	7.10	32.13
60.55	7.16	32.39

Thus the empirical formula of the resin is $(C_5H_7O_2)_n$.

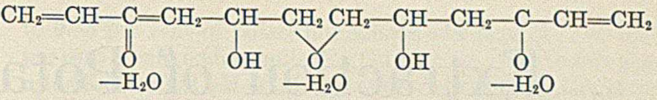
The quantitative determination of the hydroxyl groups (*6*) is based on the reaction between a solution of the substance containing hydroxyl groups and magnesium methyl iodide according to the reaction $CH_3MgI + ROH = CH_4 + ROMgI$ calculated from the formula:

$$\frac{0.000719 \times \text{cc. of } CH_4 \times \text{mol. weight of substance}}{\text{mol. weight of } CH_4 \times \text{quantity of substance}}$$

where 0.000719 = mol. weight of methane at 0° C. and 760 mm.

Taking as a basis the empirical formula of the resin $(C_5H_7O_2)$ and the molecular weight (99.05), we have, respectively, for three determinations 2.06, 1.91, and 2.01, an average of two hydroxyls. (This figure has only a relative significance because resin is not a definite chemical compound.)

The data obtained make possible the following scheme of resin formation: On one side there is formation of di- and tripolyglycerides with separation of water from two or three molecules of glycerol. On the other side acrolein is formed, which, in its turn, acts reciprocally with glycerol and polyglycerides. For example, acrolein can condense with terminal hydroxyl groups with the formation of a chainlike molecule:



$$CH_2{=}CH{-}\underset{\underset{-H_2O}{O}}{\overset{}{C}}{=}CH_2{-}\underset{OH}{CH}{-}CH_2\;\underset{\underset{-H_2O}{O}}{\vee}\;CH_2{-}\underset{OH}{CH}{-}CH_2{-}\underset{\underset{-H_2O}{O}}{C}{-}CH{=}CH_2$$

Further, the polymerization in the groups $CH_2{=}CH{-}$ is possible until a high molecular combination is obtained. To these principal products are admixed polymers of acrolein and (in raw resin) polyglycerides.

The comparison of the content of oxygen in precipitated resin (32.33 per cent) with its content in the products of condensation of glycerol with 1, 2, and 3 molecules of acrolein (36.92, 28.57, and 23.3 per cent) indicates that the resin may represent a mixture of the reaction products of glycerol and acrolein in a mean correlation between 1 and 2 molecules of acrolein to 1 molecule of glycerol. With this hypothesis in mind, the process of precipitation of hard resin from the raw material can be represented as a process of polymerization of the products of condensation of acrolein and glycerol contained in the raw resin mixed with polyglycerides and glycerol (which act as plasticizers) until solubility in water is lost. The polyglycerides remaining in the filtrate during treatment with the catalyst form anew a certain quantity of acrolein which reacts with glycerol and polyglycerides until polymerizing combinations are formed containing "resiniferous groups," forming, in their turn, hard resin when treated thermically (separation with the aid of steam).

The foregoing are as yet only hypotheses and must be confirmed by experiment.

Technical Importance of Product

The product obtained by treatment of glycerol (by heating with a catalyst) has no independent technical importance of itself. But it is of great moment in its relation to different phenol-aldehyde products of the resol or novolack type, as it gives elasticity to the phenol resins without depriving them of their primary properties. The addition of glycerol resins to phenol resins can be effected during the process of condensation, or by mixing when the product is finished.

Glycerol resins will be particularly useful for the preparation of different protective coatings (resistant to acids and to alkalies) when elasticity is of importance. Glycerol resins can also be used as plasticizers for the preparation of plastic masses of an albumin base (such as casein, albumin, leather plastics).

Literature Cited

(1) McLeod, *Am. Chem. J.*, 37, 34 (1907).

(2) Moureu, *Compt. rend.*, 169, 805 (1919); *Ann. chim.*, [9] 15, 176 (1921).

(3) Moureu, Boutaric, and Dufraisse, *J. chim. phys.*, 18, 333 (1921).

(4) Witzemann, *J. Am. Chem. Soc.*, 36, 1766 (1914).

(5) Wohl and Mylo, *Ber.*, 45, 2046 (1912).

(6) Zerewitinoff, *Z. anal. Chem.*, 50, 680 (1911).

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New Chemical Industry Established at Montreal. Halls (Canada), Ltd., a subsidiary of the Hall Chemical Co., London, England, has established a new chemical industry in Montreal by the acquisition of 43,000 square feet of property, with buildings, railway siding, and wharf on the Lachine Canal, for the purpose of manufacturing chemical products. The new company's principal product will be a rust preventive in liquid and semiliquid form, which, it is understood, is widely used by machinery makers in Great Britain for automobiles, steamships, and locomotives. Other products which the new firm will manufacture are disinfectants, a boiler-cleaning compound, refractories, iron cement, and case-hardening materials.

Much of the solid chemicals used in the manufacturing process will be imported from England, and the Canadian plant will also be given certain of the export trade now handled from England, such as the British West Indian and South American market.

Extraction of Potash from Polyhalite

III. Effect of Particle Size, Sodium Chloride Concentration, and Temperature upon Hot Extraction by a Multistage Process

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In the recovery of potassium sulfate from polyhalite by extraction of the calcined mineral with hot water, high concentrations and high recoveries in the extract liquor are desirable. Since it was believed that the optimum results might be obtained by continuous countercurrent extraction, laboratory multistage experiments simulating countercurrent operation have been performed. The effects of particle size, temperature of extraction, and sodium chloride concentration have been investigated.

The results indicate that material as coarse as −10 mesh should yield high recoveries and satisfactory concentrations at 100° C. Lower temperatures of extraction proved less favorable but the presence of a low concentration of sodium chloride was definitely favorable. Sodium chloride retards the formation of secondary solid phases in the top stage and thereby allows the attainment of higher concentrations. Using 2 parts of sodium chloride per 100 parts of water in the extraction of −10 mesh calcined polyhalite, a countercurrent procedure should give a top liquor containing from 11 to 11.5 parts of potassium sulfate per 100 parts of water with a recovery of more than 95 per cent.

The problem of recovering potash from the mineral polyhalite ($K_2SO_4 \cdot MgSO_4 \cdot 2CaOS_4 \cdot 2H_2O$), occurring in large quantities in the salt beds of Texas and New Mexico, has been under investigation at this station continuously since 1928 (see Parts I and II of this series, *7*). The experiments described in the present report were performed to ascertain whether a continuous countercurrent extraction of calcined polyhalite by hot water would yield satisfactory recoveries and concentrations of potassium sulfate in the top liquor. Previous investigation by Storch (*6*) had shown that the rate of solution of uncalcined polyhalite was too slow to be of value in an industrial process, and Storch and Clarke (*8*) had demonstrated that calcination of the polyhalite greatly accelerated the rate of solution in hot water, allowing most of the potassium sulfate to be extracted readily.

Additional experiments on the extraction of polyhalite after calcination in a small laboratory rotary kiln were reported by Clarke, Davidson, and Storch (*2*). The hot extractions were made with a ratio of two parts of water to one of polyhalite for a definite period, usually one hour, after which the solid residue was separated from the hot solution and was washed with cold water. By this procedure extractions of 85 to 95 per cent of the potash were secured with concentrations averaging from 9.5 to 10 grams of potassium sulfate per 100 grams of water. Occasionally, concentrations as high as 11 grams of potassium sulfate per 100 grams of water were obtained. Further calcination experiments on a larger scale in a 6 × 132 inch (15.2 × 335.3 cm.) gas-fired rotary kiln have been described by Conley, Fraas, and Davidson (*3*).

All of the preceding work has shown the desirability of calcining the polyhalite prior to the extraction with hot water. The extraction procedure has involved a moderate amount of agitation and a single displacement wash of the filtered residue to remove the retained extract solution. The industrial application of this means of extraction would be an intermittent or batch process.

It was thought that continuous countercurrent extraction might yield more favorable results than had been obtained in the batch experiments. A large number of extraction tests have accordingly been made with 100 to 200 gram samples of calcined Polish and Texas-New Mexico polyhalite. Owing to the difficulty of exactly simulating a continuous countercurrent process on a small scale, it has been necessary to study the extraction in several separate steps or stages. A multistage extraction process does not exactly reproduce the conditions likely to be encountered on a commercial scale, but it is believed that the data obtained furnish some insight into what may be expected from a continuous countercurrent extraction. The effects of sodium chloride concentration, particle size, and temperature of extraction were studied.

EXPERIMENTAL PROCEDURE

The apparatus used in making the multistage tests consisted of a heavy suction flask placed within a steam bath and provided with a motor-driven stirrer. A reflux condenser attached to the side tube was provided with a one-hole stopper and connections through which pressure could be applied for sample removal. The flask was fitted with a rubber stopper with a center hole for the brass stirrer which operated within a close-fitting brass sleeve. A bent glass tube for sample removal was inserted through another hole in this stopper. Evaporation losses around the stirrer were minimized by means of a rubber tube which fitted tightly around the stirrer and was attached to the brass sleeve where it extended below the stopper.

The experimental procedure in most of the countercurrent tests was essentially as follows: The desired amount of leach liquor was weighed out and placed in the flask which was then put in the steam bath and allowed to come up to temperature (95° to 96° C.). A small portion of this hot solution was then removed for analysis through the sampling tube. The flask was removed from the bath, the desired weight of calcined polyhalite was rapidly added to the flask, the flask was quickly replaced in the bath, and stirring was commenced. Samples of the resulting extract liquor were then periodically removed by applying pressure to the top of the reflux condenser, forcing a mixture of solid and liquid on to a filter. The filtered liquor was caught in a tared, glass-stoppered bottle and reserved for subsequent analysis.

If the object of the particular test was to obtain time-concentration data on the first step only, the solid residue was usually discarded. If concentrations were being studied on the second or any subsequent step, after the final liquor sample had been taken in the first stage, the extract mixture was removed from the steam bath and rapidly filtered on a Büchner funnel with the use of suction. In the meantime the liquor to be used for the next fraction was being heated in a flask provided with a reflux condenser. This solution was sampled, then quickly poured upon the warm residue obtained from the filtration. A small portion, usually 50 cc., of the fresh hot extract solution was used to wash the first residue, and this wash was combined with the previous extract. The residue with fresh extract liquor was then quickly replaced in the steam bath and extraction continued with periodic sampling as in the first step. The time required for removal of extracted mixture, filtration, and replacement generally consumed from 5 to 7 minutes.

Properties of Polyhalite Used

Owing to the scarcity of the supply of Texas–New Mexico polyhalite at the time this work was being done, most of the experiments were made on imported Polish polyhalite with physical and chemical properties similar to the American mineral. The screen analyses of the samples of polyhalite used are given in Table I, and the conditions of calcination and composition after calcination in Table II. As shown in Table II, samples 3, 5, 6, and 9 were Polish polyhalite containing varying amounts of halite (NaCl). The principal other impurity present in any appreciable quantity was anhydrite ($CaSO_4$). Samples 10 and 15 were polyhalite obtained from deposits near Carlsbad, N. Mex., and represented selected material of high purity. The chemical analysis of sample 10 indicated a composition of 97.4 per cent polyhalite, 1.05 per cent halite, and only 1.72 per cent of other impurities, principally ferric oxide, alumina, and silica. Sample 15 was of even higher purity. The chief physical difference between the Polish and the New Mexico polyhalite was that of color. Most of the Polish material was very light, almost approaching white, while the American mineral was a bright salmon pink, probably because of higher iron oxide content.

Table I. Screen Analyses of Polyhalite Used in Multistage Extraction Experiments

(In per cent by weight in fraction)

Screen Size	Sample Number 3	5	6	9	10 & 15
			before calcination		
+ 10	...	...	...	2.7	7.30
+ 20	0.10	...	...	40.8	41.80
+ 28	19.30	...	...	13.0	12.45
+ 35	...	21.10	19.05	10.0	8.33
+ 65	49.3	31.30	20.80	...	...
+100	15.6	15.27	9.27	21.2	...
+150	8.3	7.38	4.51	2.6	14.76
+250	4.2[a]	8.39	12.78	9.6[c]	1.76
+325	3.0[b]	5.09	22.04	...	13.55
−325	...	11.45	11.53	...	...
		Sample Number 5	6	9	10
			after calcination		
+ 10	...	...	...	2.61	8.25
+ 20	...	...	...	36.20	41.00
+ 35	...	19.10	17.60	22.78	20.70
+ 65	...	31.85	21.10	...	...
+100	...	14.88	9.48	22.83	13.62
+150	...	6.64	3.63	3.61	2.05
−150	...	27.51	48.22	11.97	14.40

[a] +200 screen. [b] −200 screen. [c] −150 screen.

Extraction of Calcined Polyhalite Containing Considerable Sodium Chloride by Means of Solutions High in Magnesium Sulfate and Sodium Chloride

In the earlier multistage extraction experiments the extract liquors from previous batch extractions were used as the initial leaching solutions. In these extracts the molar ratio of potassium sulfate to magnesium sulfate was nearly 1:1, with usually a slight preponderance of the latter. The actual initial concentrations in the top stage varied from 7.83 to 9.15 per cent of potassium sulfate and from 5.77 to 6.25 per cent of magnesium sulfate. Owing to the fact that syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$) always appeared as a secondary product during the extraction in the top stage, the final extract liquors contained much more magnesium sulfate than that corresponding to a 1:1 ratio.

Data from a typical experiment have been plotted in Figure 1 to show the general type of time-concentration curves obtained from the extraction of polyhalite with solutions initially containing considerable magnesium sulfate. In this particular series of tests four separate steps were used. The top three steps were carried out in the steam bath at temperatures approaching 100° C., but the final step was conducted at room temperature (20° to 25° C.) as it was originally believed that a considerable portion of the potassium sulfate in the solid at the end of the hot extraction steps was present in the form of pentasalt ($K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$) formed during the process of extraction. From the equilibrium data available (*4, 5, 10, 11*) it seemed evident that higher temperatures would be less favorable for the decomposition of this double salt.

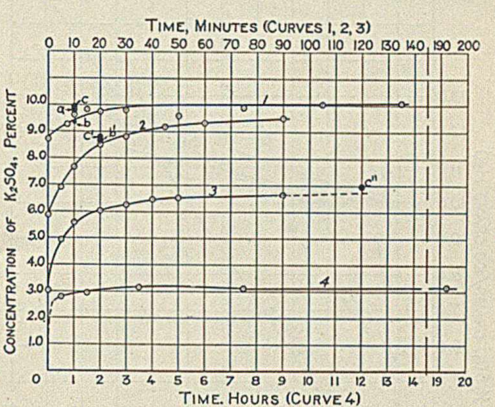

Figure 1. Changes in Potassium Sulfate Concentration during Typical Extraction of Calcined Polyhalite

Curve 1 in Figure 1 represents an extraction starting with an 8.7 per cent potassium sulfate solution. To obtain curve 2, the top- or first-stage extraction was repeated but stopped after 10 minutes at which time a concentration represented by point *a* was reached. The solid residue obtained by filtration was then treated with a 5.85 per cent potassium sulfate solution and samples were taken at the desired intervals. To obtain curve 3 the same procedure was repeated, yielding point *b* on curve 1 and *b'* on curve 2. The time-concentration data were obtained for curve 4 in an exactly analogous manner after yielding concentrations in the various stages corresponding to points *c*, *c'*, and *c''* on curves 1, 2, and 3, respectively.

The first four-stage tests were made with the relatively fine material of samples 3, 5, and 6 in Table I. Extractions of 82.6 to 85.4 per cent were obtained, as compared with values of 77.3 to 87.0 by the standard laboratory batch procedure (*2*). The over-all extraction was not essentially different in experiments 5 and 6, as compared with 3, in spite of the much higher content of fines in 5 and 6.

Table II. Calcination Data for Samples of Polyhalite Used in Multistage Extraction Experiments

Sample	3	5	6	9	10	15
Source of polyhalite	Poland	Poland	Poland	Poland	N. Mex.	N. Mex.
Size of polyhalite	−20 + 150	−30	−30	−10	−10	−10
Temp. of calcination, ° C.	454	470	460	460	460	485
Time of retention, min.	48.0	17.25	28.5	19.4	16.1	20.4
Time of calcination above 300° C., min.	36.0	13.3	20.7	13.9	11.7	16.1
Rate of calcination, lb./hr. (kg./hr.)	19.5 (8.9)	19.0 (8.6)	10.5 (4.8)	13.90 (6.30)	16.37 (7.44)	23.50 (10.70)
K_2SO_4 after calcination, %	24.60	21.78	24.53	24.70	30.20	30.37
NaCl after calcination, %	4.38	7.36	4.38	6.03	1.09	0.13
Density after calcination, grams/cc.	...	2.608	2.632	2.626	2.609	2.614
Extraction of K_2SO_4 by standard extraction, %	84.3	87.0	77.3	80.7	65.7	...

While previous extraction studies (2) made with a batch process in mind indicated that material finer than −10 mesh, preferably −28 or −30 mesh, would be desirable for best results, these limits do not necessarily apply to a countercurrent procedure where different conditions are encountered and where it would be desirable to work with material as coarse as practicable in order to facilitate separation of solid and liquid by settling. Actually, it was found that polyhalite as coarse as the −10 mesh material of samples 9 and 10 in Table II would give nearly 80 per cent extraction of potassium sulfate in the presence of appreciable quantities of sodium chloride. It was evident, however, from all of the preliminary work that the extract liquor from the top step would contain magnesium sulfate much more than equivalent to the potassium sulfate.

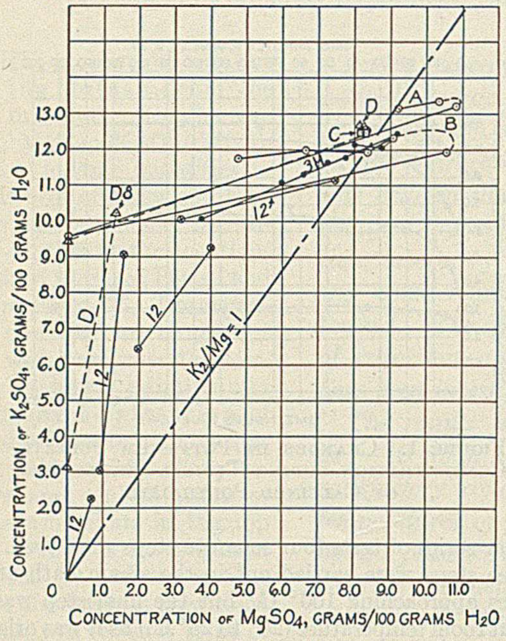

FIGURE 2. MULTISTAGE EXTRACTIONS OF −30 +150 MESH CALCINED POLYHALITE WITH SOLUTIONS CONTAINING 2 GRAMS OF SODIUM CHLORIDE PER 100 GRAMS OF WATER

EXTRACTION OF CALCINED POLYHALITE OF LOW SODIUM CHLORIDE CONTENT BY SOLUTIONS LOW IN MAGNESIUM SULFATE AND SODIUM CHLORIDE

Any leaching process which uses water alone to extract completely potassium and magnesium sulfates from calcined polyhalite must yield an extract solution in which the molar ratio of these substances will be 1:1. In the following experiments a special effort was made to manipulate the multistage extraction in such a manner as to fulfill this requirement approximately. Owing to the lack of complete understanding of the actual mechanism of the complex reactions taking place at the various stages of the process, it was necessary to select arbitrarily initial liquors of different potassium sulfate and magnesium sulfate content and, by using varying amounts of these solutions, to make a number of extraction tests until the proper conditions were secured. By repeated trials the initial concentration of the magnesium sulfate in the first stage was gradually lowered until the end solutions after extraction yielded the desired 1:1 molar ratio of potassium sulfate to magnesium sulfate. It was found that only a small percentage of magnesium sulfate could be present in the initial solutions used for extracting freshly calcined polyhalite in the top step.

EFFECT OF SODIUM CHLORIDE UPON EXTRACTION. The Polish polyhalite used in the earlier experiments contained appreciably larger amounts of sodium chloride than sample 10, representing the first domestic polyhalite tested during this investigation. It was while attempting to extract this latter sample of polyhalite from the New Mexico deposits that the importance of the presence of sodium chloride during extraction was discovered. In order to compare the results of the New Mexico polyhalite with those previously obtained with the Polish mineral, sample 10 was screened into several sizes. The +10, −10 +20, −30 +35, −35 +150, and −150 fractions, as well as the composite sample, were extracted by the standard batch extraction procedure, yielding the values shown in Table III. The first six tests with the sized fractions and composite of the New Mexico polyhalite gave low concentrations and poor extractions. An increase in the ratio of water to potassium sulfate from 6.93 to 7.96 in an extraction of the composite material merely decreased the concentration without improving the percentage extraction. However, the last two standard extraction tests made at the same time, with equal ratios of water to potassium sulfate, same length of time for extraction, and other conditions comparable, but with 5 and 10 grams of sodium chloride, respectively, added to the solid just prior to its addition to the boiling water, yielded much higher recoveries and concentrations.

TABLE III. EFFECT OF PARTICLE SIZE AND ADDITION OF SODIUM CHLORIDE UPON STANDARD BATCH EXTRACTION OF NEW MEXICO POLYHALITE

FRACTION SIZE	CONCN. OF EXTRACT LIQUOR	EXTRACTION OF K_2SO_4	EXTRACTION RATIO $H_2O:K_2SO_4$	NaCl ADDED
	G. K_2SO_4/100 g. H_2O	%		*Grams*
+10	7.98	54.5	6.93	0
−10 +20	8.90	60.7	6.93	0
−20 +35	8.59	57.7	6.93	0
−35 +150	9.26	65.4	6.93	0
−150	7.30	50.2	6.93	0
Composite	9.47	65.5	6.93	0
Composite	8.26	65.7	7.96	0
Composite	10.20	80.8	7.96	5
Composite	10.84	85.8	7.96	10

An attempt was made to determine the effect of the sodium chloride content during the first stage of the countercurrent extraction in order to obtain some information on the mechanism of the reactions taking place. Two extractions of −35 +150 mesh calcined polyhalite containing 30.37 per cent of potassium sulfate and 0.35 per cent of sodium chloride were made in as nearly the same manner as possible, but a quantity of sodium chloride corresponding roughly to 3 grams per 100 grams of water was added to test A, while no addition was made to test B. The initial potassium sulfate concentration of the solution used for extraction was 8.7 per cent, a concentration used in the top stage of many of the countercurrent tests. A low ratio of water to potassium sulfate of 6.08 was used in order to obtain high concentrations of potassium sulfate and magnesium sulfate. In these tests the calcined polyhalite was added to the boiling potassium sulfate solution in a flask provided with a reflux condenser. There was no agitation other than that due to ebullition. Samples of the liquid and solids were removed periodically for chemical and petrographic analysis at the time intervals indicated.

The time-concentration data obtained in these tests are given in Table IV; in Table V the various solid phases found by petrographic examination are compared with the amounts of these substances indicated by the concentration changes in the liquid phase. The petrographic data definitely prove the presence of both polyhalite and syngenite and agree with the chemical data in indicating an increase in polyhalite at the expense of the syngenite which was formed initially in large quantities.

Table IV. Effect of Sodium Chloride on Concentrations of Solutions in First-Stage Extraction of −35 +150 Mesh Calcined Polyhalite[a]

Test	Step	Time	Concentration of Extract: K_2SO_4		$MgSO_4$		NaCl	
		Min.	%	G./100 g. H_2O	%	G./100 g. H_2O	%	G./100 g. H_2O
A0	1	0	8.70	9.52	0	0	0	0
1		30	10.40	13.23	8.49	10.80	2.49	3.17
2		60	10.50	13.32	8.16	10.35	2.49	3.16
3		120	10.50	13.19	7.34	9.22	2.56	3.23
B0		0	8.70	9.52	0	0	0	0
1		30	9.74	11.92	8.63	10.58	..	0.19[b]
2		45	10.15	12.32	7.45	9.04	..	..
3		60	9.91	11.93	6.93	8.33	..	..
4		90	10.10	12.00	5.57	6.61	..	..
5		120	10.08	11.73	4.04	4.72	..	..
C1		0	8.64	9.45	0	0		0
2		30	10.16	12.50	6.76	8.32	1.82	2.24
3		45	10.18	12.50	6.64	8.15	1.83	2.25
D1	1	0	8.64	9.45	0	0	0	0
2		30	10.28	12.65	6.68	8.22	1.83	2.25
3		45	10.32	12.70	6.58	8.10	1.85	2.27
4	2	0	3.07	3.17	0	0	0	0
5		90	8.65	...	..	...	..	..
6		120	8.82	...	..	...	..	..
7		180	9.16	...	..	...	..	..
8		240	9.17	10.25	1.18	1.32	0.27	0.30

[a] Polyhalite contained 30.37% K_2SO_4 and 0.35% NaCl. Ratio of H_2O to K_2SO_4 for extraction was 6.08.

[b] Computed.

Tests C and D in Table IV represent top-stage extractions of this same material with solutions containing 9.45 grams of potassium sulfate and 2.25 grams of sodium chloride per 100 grams of water. Samples were taken after 30 and 45 minutes, and in D the solid residue from the 45-minute, first-stage extraction was also recovered and put through a second-stage hot extraction.

The chemical data for these tests, which are plotted in Figure 2, show that higher concentrations of potassium sulfate and magnesium sulfate were obtained in the presence of sodium chloride in test A than in its absence in test B, indicating that secondary reactions by which both of these substances are removed from solution were much less active in A. The trend of the concentrations in test B, to which no sodium chloride was added, would indicate that the rapid decrease in magnesium sulfate concentration was undoubtedly due to the formation of polyhalite, as would be expected since the liquid-phase compositions are definitely in the polyhalite field at 100° C. immediately after the extraction begins (*9*). The rate of formation of polyhalite in test A in the presence of salt is markedly lower. It is evident in both cases that large amounts of syngenite are formed as soon as the calcined polyhalite is added to the hot potassium sulfate solution but that this unstable phase gradually decomposes as the stable polyhalite is formed.

Extractions with −30 +150 Mesh Material. The results of extracting the −30 +150 mesh calcined polyhalite of sample 3H to yield a final solution of moderately high sodium chloride content are shown graphically in Figure 2. The maximum concentration of potassium sulfate reached in this test was approximately 12.5 grams per 100 grams of water, but it should be pointed out that the sodium chloride content was as high as 3.25 grams per 100 grams of water. The molar ratio of potassium sulfate to magnesium sulfate closely approximated the ideal of 1:1 after the 20-minute sample.

A four-stage extraction of −30 +150 mesh, washed New Mexico polyhalite, calcined one hour in the stationary-tube electric furnace at a temperature between 300° and 480° C., but at the higher temperature for most of the time, is also shown graphically in Figure 2 as sample 12. While the various steps did not meet each other exactly, it is important to note that a top liquor concentration of more than 11 grams of potassium sulfate per 100 grams of water was obtained with an extraction of 97 per cent as determined by analysis of the solid residue from the fourth step.

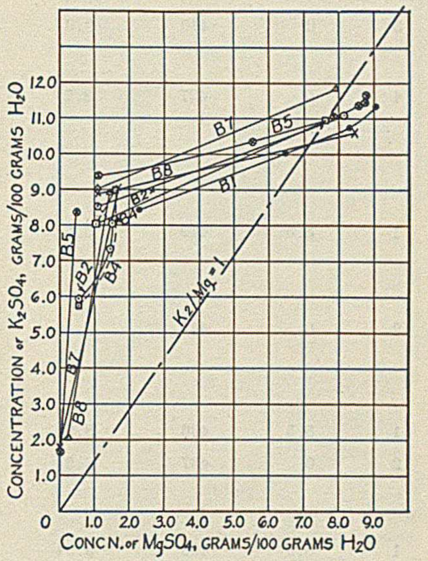

Figure 3. Multistage Extractions of −10 Mesh Calcined Polyhalite with Solutions Containing 2 Grams of Sodium Chloride per 100 Grams of Water

Extraction of −10 Mesh Material. That equally as good results might be obtained on coarser material was shown by an extraction of −10 mesh polyhalite from the same lot as sample 10. The polyhalite was calcined in the 2-inch (5-cm.) laboratory rotary furnace (*2*) for a total of 28 minutes above 300° with an average maximum of 484° C. during most of the calcination. In this experiment, sufficient sodium chloride was added to give a concentration of approximately 2 grams per 100 grams of water. The concentration of the top extract liquors was nearly 11 grams of potassium sulfate per 100 grams of water, and the percentage extraction was about 99 per cent.

During a series of tests on the −10 mesh material represented by sample 15, data for which are given in Table VI and plotted in Figure 3, the sodium chloride content was again adjusted to be approximately equivalent to 5 per cent halite

Table V. Correlation of Results of Petrographic Examination with Calculated Composition of Solid Residues from Extraction Process

Sample	Time	Composition of Residues Calcd. from Soln. Data: Polyhalite	Syngenite	$CaSO_4$[a]	Solid Phases Indicated by Petrographic Examination[b]
	Min.	%	%	%	
A1	30	7.08	55.56	37.36	Original polyhalite incompletely extracted. Large amounts of syngenite. Anhydrite.
2	60	14.24	50.55	35.21	Original polyhalite incompletely extracted, and new crystals of polyhalite beginning to form from solution. Large amount of syngenite, about the same as preceding sample. Anhydrite.
3	120	26.98	42.23	30.79	Polyhalite forming from solution. Syngenite still present in large amounts, but less than in preceding sample.
B1	45	28.4	43.6	28.0	Original polyhalite incompletely decomposed. Large amount of syngenite. Anhydrite.
2	90	52.4	27.9	19.7	New crystals of polyhalite forming from solution. Syngenite corroded, smaller amount than in preceding sample.
3	120	68.8	17.2	14.0	Polyhalite forming from solution in large quantities. Syngenite corroded, smaller amount than in preceding sample. Anhydrite less than in preceding sample.

[a] Present both as anhydrite and as undetermined form left as residue during extraction of polyhalite.

[b] Petrographic examination by A. Gabriel, assistant chemist-petrographer, Nonmetallic Minerals Experiment Station.

TABLE VI. MULTISTAGE EXTRACTION OF −10 MESH POLYHALITE WITH ADDED SODIUM CHLORIDE BY SOLUTIONS LOW IN MAGNESIUM SULFATE AND SODIUM CHLORIDE[a]

Expt.	Step	NaCl Added	Water Added	$H_2O:K_2SO_4$	Time	Concentration of Extract					
						K_2SO_4		$MgSO_4$		NaCl	
		Grams	Grams		Min.	%	G./100 g. H_2O	%	G./100 g. H_2O	%	G./100 g. H_2O
15B1	1	7.2	398	9.2	0	7.62	8.44	2.06	2.28	0	0
					5	8.47	10.02	5.48	6.46	1.59	1.88
					15	8.89	10.72	6.82	8.24	1.54	1.86
					30	9.28	11.35	7.36	9.05	1.57	1.92
15B2	1	9.0	473.2	9.1	0	7.78	8.52	1.00	1.10	0	0
					30	9.15	11.10	6.70	8.13	1.73	2.10
	2	0	485	9.3	0	5.60	5.96	0.50	0.53	0	0
					15	6.32	...	..	..	..	..
					30	6.71	7.31	1.33	1.45	0.14	0.15
					60	7.30	8.01	1.37	1.50	0.13	0.14
15B4	1	8.5	448	9.15	0	7.39	8.02	1.00	1.09	0	0
					30	8.90	...	..	..	..	..
					45	9.10	10.97	6.30	7.59	1.69	2.04
	2	0	420	8.6	0	5.76	6.14	0.50	0.53	..	..
					90	8.14	9.00	..	1.51[b]	..	..
	3	0	440	9.0	0	3.06	3.20	0.25	0.26	..	..
					10	5.56	5.87[b]	..	..	..	..
					20	6.36	6.78[b]	..	..	..	..
					30	6.68	7.22[b]	..	..	..	..
	4	0	427	8.7	0	0	0	..	..	..	..
					15	1.78	1.81[b]	..	..	..	..
					30	1.84	1.88[b]	..	..	..	..
					60	2.14	2.19[b]	..	..	..	..
					90	2.36	2.42[b]	..	..	..	..
					120	2.42	2.48[b]	..	..	..	..
					183	2.61	2.68[b]	..	..	..	..
					240	2.64	2.71[b]	..	..	..	..
15B5	1	8.5	419	8.6	0	8.50	9.40	1.00	1.10	0	0
					5	8.80	10.34	4.73	5.55	1.38	1.62
					15	9.19	11.08	6.50	7.84	1.37	1.65
					30	9.36	11.38	7.06	8.59	1.37	1.67
					45	9.41	11.44	7.16	8.72	1.39	1.69
					60	9.52	11.66	7.13	8.73	1.61	1.97
	2	0	415	8.46	0	1.60	1.63	..	0	..	..
					34	7.25	...	..	..	..	..
					64	7.62	...	..	..	..	..
					94	7.77	...	..	..	..	..
					120	7.75	...	..	..	..	..
					160	7.65	8.34[b]	..	0.47[b]	..	..
5B7	1	8.5	436	8.9	0	8.25	9.09	1.00	1.10	0	0
					45	9.72	11.85	6.48	7.90	1.77	2.16
	2	0	437	8.9	0	2.00	2.05	0.23	0.24	0	0
					10	5.86	...	..	..	..	..
					30	7.12	...	..	..	..	..
					60	7.82	...	..	..	..	..
					90	8.10	8.94	1.30	1.44	..	..
15B8	1	8.5	438	8.94	0	8.09	8.90	1.00	1.10	..	..
					45	8.90	10.60	7.07	8.41	1.75	2.08
	2	0	438	8.84	0	1.70	1.73	0	0	..	..
					60	7.42	...	..	..	..	..
					120	8.08	...	..	..	..	..
					180	8.12	9.02	1.51	1.68	0.33	0.37

[a] Calcined polyhalite contained 30.37% K_2SO_4 and 0.13% NaCl. Charge used was 161.5 grams in all tests excepting B1 and B2 in which 142.8 and 171.5 grams, respectively, were used.

[b] Computed.

in the original raw polyhalite. Tests 15B1 on the first stage and 15B2 on the first and second stages were exploratory. Tests 15B3 and 15B4 were made by the use of three successive hot extraction steps as in some of the earlier countercurrent experiments, but, as the data accumulated, it was noted that the concentration of the extracts from the second and third steps closely approximated each other, so that but two hot extraction steps were used in all later tests.

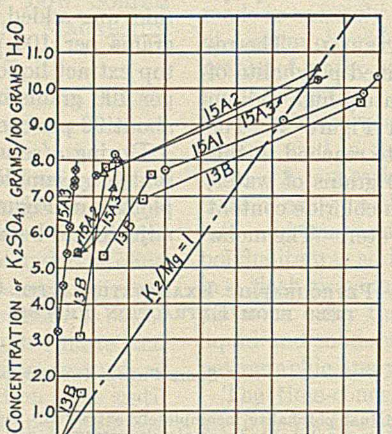

FIGURE 4. MULTISTAGE EXTRACTIONS OF −10 MESH CALCINED POLYHALITE WITH SOLUTIONS PRACTICALLY FREE FROM SODIUM CHLORIDE

Test 15B4 shows a fairly well-balanced example of the four-stage extraction procedure, in which each stage yielded a solution close to the concentration of the starting solution for the preceding stage. The concentration of 11 grams of potassium sulfate per 100 grams of water in the extract liquor from the first stage stands in the proper relation to the ratio of water to potassium sulfate ratio of 9.15, to give a very high recovery, and the molar ratio of potassium sulfate to magnesium sulfate has the proper value of 1:1.

Tests 15B5, 15B6, and 15B7 were made to secure a properly balanced system by the use of two hot extraction steps. Test 15B7 shows reasonably good results, with the proper concentrations and satisfactory coördination of the second with the first step. Test 15B8 was made to determine if any advantage would accrue by a slightly longer time of extraction in the second step. No improvement was obtained by increasing the time from 90 to 180 minutes. All of these tests indicate that a high degree of extraction should be possible with a concentration in the top liquor of about 11 grams of potassium sulfate per 100 grams of water, and that material as coarse as −10 mesh should be easily treated. Actual percentage recoveries have not been determined on this material, but, by comparison with results on the finer material, no difficulty would be anticipated in obtaining satisfactory results.

EXTRACTION OF CALCINED POLYHALITE OF LOW SODIUM CHLORIDE CONTENT BY SALT-FREE SOLUTIONS

The presence of appreciable amounts of sodium chloride in the extract liquors might be a disadvantage in some cases. Accordingly, in order to determine the results which might be obtained in the absence of sodium chloride, a number of extraction experiments was made upon calcined New Mexico polyhalite which had been washed with water prior to calcination until it was practically free from sodium chloride. No sodium chloride was added to the extract solutions in this series.

From previous batch experiments in the laboratory it had been generally observed that the use of higher ratios of water to potassium sulfate resulted in a better percentage extraction, usually at a sacrifice in the concentration. A relatively low initial concentration of potassium sulfate and a relatively high ratio of water to potassium sulfate of approximately 10 were used in test 13B, the results for which are shown graphically in Figure 4. In this test 96 per cent of the potassium sulfate was extracted with a top concentration of 9.66 grams of potassium sulfate per 100 grams of water. One noticeable effect of the high ratio of water to potassium sulfate was the increased solution of the magnesium sulfate content of the charge in the top step.

A number of additional multistage leaching tests was made upon a sample of −10 mesh material taken from lot 15, washed prior to calcination in order to reduce the salt content to 0.13 per cent sodium chloride, and calcined in the 6-inch (15.3-cm.) rotary furnace (*3*) at 484° C. The details of extraction have been summarized in Table VII and the results plotted in Figure 4. In the absence of sodium chloride but with fairly high ratios of water to potassium sulfate, concentrations of the order of 10 grams of potassium sulfate and 7 grams of magnesium sulfate per 100 grams of water, combined with satisfactory recoveries, seem possible for material as coarse as −10 mesh.

TABLE VII. MULTISTAGE EXTRACTION OF −10 MESH POLYHALITE WITH NO ADDITION OF SODIUM CHLORIDE WITH SOLUTIONS LOW IN MAGNESIUM SULFATE[a]

Expt.	Step	Water Added	H_2O: K_2SO_4	Time	Concentration of Extract: K_2SO_4		$MgSO_4$	
		Grams		*Min.*	%	*G./100 g. H_2O*	%	*G./100 g. H_2O*
15A1	1	388.6	9.5	0	7.01	7.72	2.09	3.00
				5	7.91	9.12	5.46	6.30
				15	8.31	9.86	7.21	8.54
				30	8.66	10.32	7.51	8.95
				45	8.91	...	..	..
				60	8.62	...	..	..
				90	8.72	...	..	..
15A2	1	407.9	9.9	0	7.00	7.63	1.14	1.24
				30	8.94	10.52[b]	..	7.16[b]
	2	407	9.9	0	5.15	5.46	0.50	0.53
				5	5.98	...	..	..
				15	6.66	7.25	1.42	1.55
				30	6.94	...	..	..
				45	7.31	8.01	1.41	1.55
15A3	1	437	9.6	0	6.99	7.60	1.00	1.09
				30	8.71	10.20	6.17	7.23
	2	437	9.6	0	5.14	5.45	0.50	0.53
				45	7.37	8.08[b]	..	1.61[b]
	3	456	10.0	0	3.17	3.27[b]	..	..
				10	4.31	4.50[b]	..	..
				20	5.14	5.42[b]	..	..
				30	5.80	6.16[b]	..	..
				45	6.35	6.78[b]	..	..
				60	6.51	6.96[b]	..	..
				90	7.04	7.58[b]	..	..
				120	7.16	7.71[b]	..	..

[a] Calcined polyhalite contained 30.37% K_2SO_4 and 0.13% NaCl; 135-gram charges used in A1 and A2, 150 grams in A3.
[b] Computed.

EFFECT OF TEMPERATURE DURING EXTRACTION. Since all of the previous extractions of calcined polyhalite by the multistage process were made at temperatures approximating 100° C., it was deemed worth while to check the extraction at lower temperatures. A separate series of tests was accordingly made in a flask provided with a mechanical stirrer and maintained at the desired temperature by immersion in an automatically regulated water thermostat. The sample of calcined polyhalite used was a −35 +150 mesh fraction of a high-grade New Mexico polyhalite containing 30.37 per cent of potassium sulfate and 0.35 per cent of sodium chloride after calcination. Using pure water as the initial extracting solution, time-concentration determinations were made at 80°, 90°, and 101–102° C., respectively. The results given in Table VIII and shown graphically in Figure 5 clearly indicate that higher temperature favors a more rapid rate of approach to the maximum concentration and that this maximum also increases with temperature.

In addition to the straight water extractions at the various temperatures, two-stage extraction experiments were made in which the first step was extracted at 101° to 102° C., and the second steps at 80° and 90° C., respectively. These tests likewise showed a slower rate of increase in concentration in the second stage and, in general, yielded lower maximum concentrations than had previously been secured at 100° C. From the results of these tests it would seem that temperatures below 100° C. are not desirable during the top extraction stages.

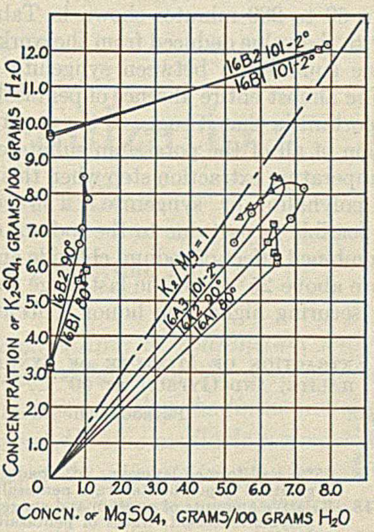

FIGURE 5. EFFECT OF TEMPERATURE UPON SINGLE- AND MULTISTAGE EXTRACTIONS OF −35 +150 MESH CALCINED POLYHALITE WITH SOLUTIONS PRACTICALLY FREE FROM SODIUM CHLORIDE

TABLE VIII. EFFECT OF TEMPERATURE ON SINGLE-STAGE EXTRACTION AND ON SECOND STAGE OF MULTISTAGE EXTRACTION OF −35 +150 MESH, CALCINED POLYHALITE[a]

Expt.	Step	Temp.	H_2O: K_2SO_4	Time	Concentration of Extract: K_2SO_4		$MgSO_4$	
		° C.		*Hours*	%	*G./100 g. H_2O*	%	*G./100 g. H_2O*
16A1	1	80	9.87	1	5.41	6.09	5.78	6.50
				2	5.58	6.29	5.75	6.48
				3	5.63	6.35	5.72	6.45
				4	6.31	7.17	5.63	6.39
				5	5.90	6.66	5.51	6.22
16A2	1	90	9.87	0.75	6.41	7.32	6.00	6.86
				1.75	7.10	8.19	6.26	7.23
				3	7.06	8.07	5.50	6.29
				6	6.59	7.46	5.08	5.75
				11	5.93	6.63	4.68	5.24
16A3	1	101–2	9.87	0.5	7.36	8.46	5.69	6.54
				0.75	7.39	8.49	5.57	6.40
				1	7.05	8.06	5.48	6.27
				1.5	6.89	7.84	5.27	6.00
				2	6.76	7.66	5.02	5.69
				3	6.53	7.36	4.80	5.41
16B1	1	100	8.16	0	8.80	9.65	0	0
				25[b]	10.06	12.04	6.40	7.66
	2	80	8.16	0	3.11	3.21	0	0
				1	5.21	5.54	0.77	0.82
				2	5.34	...	..	..
				3	6.03	...	..	..
				4	5.95	...	..	..
				5	5.47	5.84	0.98	1.05
16B2	1	101–2	8.16	0	8.75	9.59	0	0
				27[b]	10.16	12.20	6.57	7.89
	2	90	8.16	0	3.16	3.26	0	0
				1.5	6.14	6.60	0.76	0.82
				3	6.50	7.02	0.85	0.92
				5	7.75	8.48	0.87	0.95
				22	7.21	7.85	0.98	1.07

[a] Calcined polyhalite contained 30.37% K_2SO_4 and 0.35% NaCl.
[b] Minutes.

A single last-stage extraction of a residue similar to that obtained from the hot extraction stages has been made at a temperature other than the room temperature of approximately 25° C. This extraction was made at 50° C. upon a synthetic mixture of syngenite, polyhalite, and gypsum by means of water containing 2.28 per cent of sodium chloride. The mixture used in the extraction corresponds roughly to one which would occur in the large-scale extraction of polyhalite by the countercurrent process. The concentrations at times from 60 to 280 minutes shown in Table IX correspond closely to the value deduced from the work of Barre (*1*) for metastable equilibrium between syngenite and gypsum at 50° C. The almost entire absence of pentasalt in the final residue is important in that it suggests the possibility of complete extraction of all of the potassium sulfate coming down to the low-temperature extraction step when this is present as unextracted polyhalite or syngenite. The concentration reached was possible in part due to the sodium chloride content. The combined effect of sodium chloride and of increase in temperature above 25° C. in the last stage should materially assist in securing higher top liquor concentrations.

TABLE IX. EXTRACTION OF MIXTURE OF SYNGENITE, POLYHALITE, AND GYPSUM AT 50° C.[a]

TIME *Min.*	K_2SO_4 %	NaCl %	PETROGRAPHIC DATA
0	0	2.28	
10	4.06	2.18	95% well-formed gypsum, 5% badly corroded syngenite, 1% polyhalite, trace pentasalt and anhydrite
20	4.22	2.18	Relative amounts of gypsum and syngenite unchanged, polyhalite absent, traces of pentasalt and anhydrite
60	4.32	2.17	98–99% gypsum, 1–2% syngenite, trace of pentasalt
90	4.30	2.17	....
120	4.34	2.19	+99% gypsum, traces syngenite and pentasalt
280	4.32	2.18	Same as preceding sample

[a] Initial mixture contained (gram): syngenite 45, polyhalite 10, gypsum 165, water 600, and NaCl 13.

SUMMARY AND CONCLUSIONS

During a series of multistage extractions of calcined polyhalite in which a countercurrent system was simulated, the effects of particle size, temperature of extraction, and sodium chloride concentration of the extracting liquor have been investigated.

Experiments with material of different size ranges indicate that satisfactory concentrations and recoveries of potassium sulfate may be obtained on −35 +100 mesh, −20 mesh, and even on −10 mesh polyhalite. In general, the coarser the material the longer the time required to attain maximum concentrations in the first step. Secondary reactions which tend to remove potassium sulfate from solution are less serious when the coarser calcined polyhalite is extracted. The results show that material as coarse as 10 mesh should be suitable for use in a countercurrent process.

The tests show that temperatures approaching the boiling point are desirable in all stages of the extraction system, excepting the final stage. Temperatures approximating 25° C. were used in the final extraction step, but it is possible that a somewhat higher temperature should be used, since in the presence of a low concentration of sodium chloride both syngenite and polyhalite were decomposed at 50° C. without the formation of any pentasalt to yield a solution containing 4.3 grams of potassium sulfate per 100 grams of water.

The presence of sodium chloride has been definitely proved to be advantageous in securing higher concentrations and recoveries of potassium and magnesium sulfates during the hot extraction steps. The amount of sodium chloride that may be used is limited, since high concentrations decrease the subsequent recovery of potassium sulfate in certain proposed processes involving the evaporation of the extract liquors. No special difficulty is encountered unless the sodium chloride in the polyhalite exceeds one-fifth of the amount of potassium sulfate present. This quantity of sodium chloride will yield an extract containing from 2 to 2.5 grams of sodium chloride per 100 grams of water, a concentration sufficiently high for good results during extraction.

By a correlation of chemical and petrographic data obtained on a number of the experiments, it is possible to explain the mechanism of the extraction process. The concentrations of potassium sulfate and magnesium sulfate obtained at any time are the net result of two competitive actions: (1) the solution of the soluble components from the calcined polyhalite tending to raise the concentrations and (2) the formation of secondary reaction products tending to decrease the concentrations. When material of fine particle size is extracted, the rate of solution is rapid, but the rate of formation of secondary products is also accelerated. Extractions at temperatures lower than 100° C. show a decrease in the rate of solution without material change in the rate of formation of secondary double salts. Coarse material dissolves more slowly and appears to favor a slower rate of formation of secondary products.

Visual, chemical, and petrographic evidence show that, when calcined polyhalite is added to a hot potassium sulfate solution, as in the first stage of the countercurrent extraction, voluminous quantities of syngenite are immediately formed. Petrographic and chemical data also prove that, as the extraction is prolonged, polyhalite appears as a new solid phase and the syngenite originally formed begins to redissolve. This phenomenon is due to the fact that polyhalite is the stable solid phase under the conditions of the top stage of the extraction system. Apparently the formation of polyhalite and decomposition of syngenite proceed simultaneously. Sodium chloride retards the formation of secondary polyhalite and probably decreases the rate of formation of syngenite. It is known that sodium chloride increases the equilibrium concentration of potassium sulfate at 25° C. when syngenite and gypsum are the stable phases. There is some evidence to indicate a similar effect at 100° C. in the top stage of the extraction, resulting in a lessened tendency toward the formation of metastable syngenite.

The second and third stages in the earlier tests and the second stage only in the latter tests represent the rapid decomposition of the syngenite formed in the first step and the further solution of calcined polyhalite not dissolved in the top step. This solution and decomposition of syngenite is effected without any appreciable formation of pentasalt ($K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$), permitting the ultimate removal of practically all of the potassium sulfate originally present. The conditions which favor the formation of either polyhalite or pentasalt are to be avoided, since but moderate amounts of either product may be decomposed in the last or final step of the extraction process with the amount of water available.

The final step of the extraction process represents the decomposition of any residual syngenite not dissolved in the previous steps, together with the solution of a portion of the secondary polyhalite and any pentasalt present. The actual amounts of pentasalt observed in the residues from the hot extraction steps have been exceedingly small.

The recoveries and optimum concentrations that may be expected to result from the countercurrent extraction of −10 or −20 mesh calcined polyhalite will depend to some extent on the amount of sodium chloride present. Higher concentrations as well as better recoveries of potassium sulfate will be more readily obtained when sodium chloride is present. It is the opinion of the authors that concentrations of 11 to 11.5 grams of potassium sulfate per 100 grams of water with recoveries as high as 97 to 98 per cent should be possible in the presence of 2 to 2.5 grams of sodium chloride per 100 grams of water. In the absence of sodium chloride or with but small amounts, both the concentrations and recoveries will be lower.

LITERATURE CITED

(1) Barre, *Compt. rend.*, 148, 1604–6 (1909); *Ann. chim. phys.*, 24, 145–256 (1911).
(2) Clarke, Davidson, and Storch, Bur. Mines, *Rept. Investigations* 3061 (1931).
(3) Conley, Fraas, and Davidson, *Ibid.*, 3167 (1932).
(4) D'Ans, *Z. anorg. allgem. Chem.*, 62, 129–67 (1909).
(5) International Critical Tables, Vol. IV, p. 353, McGraw-Hill, 1926.
(6) Storch, Bur. Mines, *Rept. Investigations* 3032 (1930).
(7) Storch, IND. ENG. CHEM., 22, 934 (1930); Storch and Fragen, *Ibid.*, 23, 991 (1931).
(8) Storch and Clarke, Bur. Mines, *Rept. Investigations* 3002 (1930).
(9) Unpublished data obtained at this station (to be submitted for publication during 1933).
(10) Van't Hoff, Voerman, and Blasdale, *Sitzber. preuss. Akad. Wiss.*, 1905, 305.
(11) Van't Hoff, and Wilson, *Ibid.*, 1900, 1142.

RECEIVED February 28, 1933. Presented before the Division of Industrial and Engineering Chemistry at the 85th Meeting of the American Chemical Society, Washington, D. C., March 26 to 31, 1933. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

Reactions during Vulcanization

III. The Multiple-Accelerator Effect[1]

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Diphenylguanidine functions as an activator for mercaptobenzothiazole when the two accelerators are compounded in a stock deficient in fatty acids. Diphenylguanidine functions as an accelerator when compounded with mercaptobenzothiazole in a stock with a normal fatty acid content.

Butyraldehyde aniline in conjunction with mercaptobenzothiazole behaves in the same manner as diphenylguanidine. Within the limits investigated, the amount of soluble zinc available for reaction has a direct bearing on the ultimate tensile strength of diphenylguanidine and mercaptobenzothiazole stocks.

TECHNICAL interest in the two-accelerator or multiple-accelerator effect has received considerable impetus within the past several years owing to improvements in factory processing methods which permit the utilization of its advantages. However, the literature records very little of scientific interest on the phenomenon.

TWO-ACCELERATOR EFFECT

The salient facts are well known. Perhaps the most common example is the combination of mercaptobenzothiazole and diphenylguanidine. From Figure 1 it is evident that a mixture of 0.5 per cent of mercaptobenzothiazole and 0.5 per cent of diphenylguanidine is a more effective accelerator than one per cent of either accelerator alone. The presence of stearic acid in the mercaptobenzothiazole formula and its omission with diphenylguanidine is to the advantage of each accelerator, as will be shown later.

Whitby and Cambron (*5*), in seeking an explanation for this phenomenon, came to the conclusion that the soaps formed by the reaction of the basic accelerator and the resin acids in rubber functioned as very active dispersing agents and would assist in the reaction between caoutchouc and sulfur during vulcanization. Although it may be that Whitby and Cambron's explanation has some bearing on vulcanization, it obviously has definite limitations because it could not apply in the case of two accelerators of the acidic type, such as tetramethylthiuram disulfide with mercaptobenzothiazole, a combination of which shows the two-accelerator effect.

As a result of some experimental work with the accelerator mixture, diphenylguanidine and mercaptobenzothiazole, a partial explanation of the two-accelerator effect suggests itself. In a stock deficient in fatty acids (contains 40 per cent as much fatty acid as first quality rubber) accelerated with 0.5 per cent of mercaptobenzothiazole, increments of diphenylguanidine increase the tensile strength (Figure 2*A*). When the same base stock is accelerated with 0.5 per cent of diphenylguanidine, and increments of mercaptobenzothiazole are added, the rate of cure increases as shown by the decreased time to the optimum cure, despite the fatty acid deficiency of the stock (Figure 2*B*). Where there is a deficiency in fatty acids, diphenylguanidine renders the zinc oxide effective for the activation of the second accelerator (mercaptobenzothiazole), performing the same function as the fatty acids, if they were present. These results are in agreement with the observations of Sebrell and Vogt (*4*) that all accelerators require soluble zinc to produce the best physical properties and that diphenylguanidine reacts directly or through some sulfur reaction products to render zinc oxide soluble for activation.

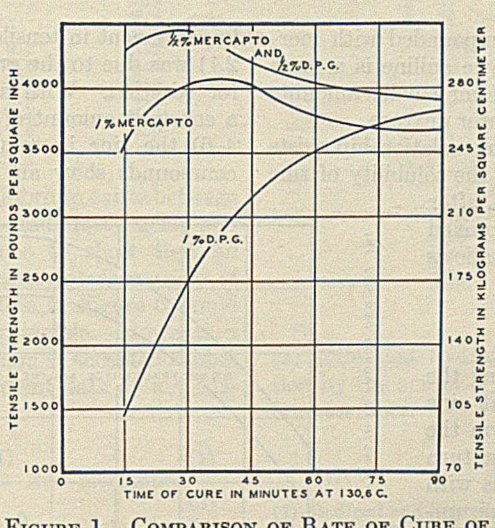

FIGURE 1. COMPARISON OF RATE OF CURE OF MERCAPTOBENZOTHIAZOLE, DIPHENYLGUANIDINE, AND MIXTURES OF THE TWO

FORMULA

Pale crepe	100	100	100
Stearic acid	...	3.0	...
Mercaptobenzothiazole	0.5	1.0	...
Diphenylguanidine	0.5	...	1.0
Zinc oxide	12.2	12.2	12.2
Sulfur	3.0	3.0	3.0

Three per cent of stearic acid was added to each of the series of stocks described above. In the first series

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[1] Part I, IND. ENG. CHEM., 23, 1467 (1931); Part II, *Ibid.*, 24, 565 (1932).

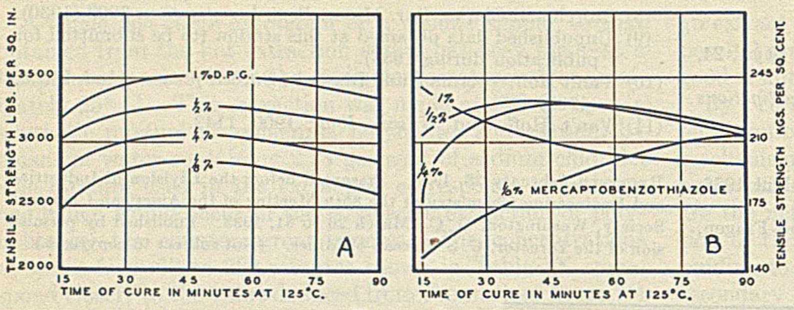

FIGURE 2

	A	B
Rubber deficient in fatty acids	100	100
Mercaptobenzothiazole	0.5	Variable
Diphenylguanidine	Variable	0.5
Zinc oxide	12.2	12.2
Sulfur	3.0	3.0

in which mercaptobenzothiazole was held constant at 0.5 per cent, increments of diphenylguanidine increase the rate of cure (Figure 3*A*). Likewise when corresponding amounts of mercaptobenzothiazole were added to the second series with 0.5 per cent of diphenylguanidine (Figure 3*B*), the rate of cure was increased. These experiments indicate that in the presence of fatty acids, a mixture of diphenylguanidine and mercaptobenzothiazole forms a new accelerator which is much more active than either one alone. Therefore, it is clear that diphenylguanidine in the presence of mercaptobenzothiazole has a dual action, functioning as an activating agent in the absence of fatty acids and as an accelerator when these materials are already present.

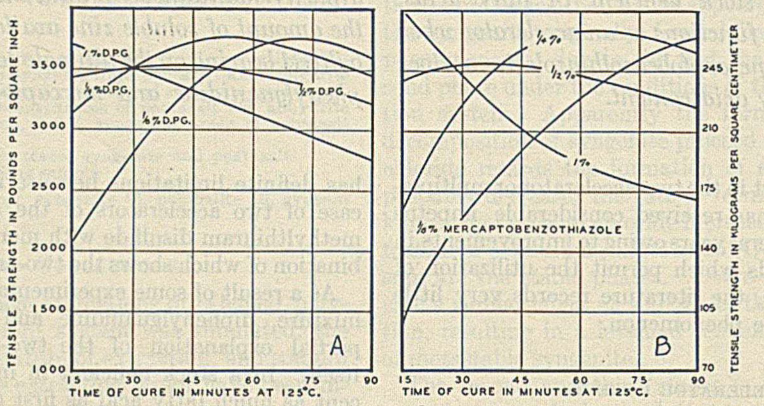

FIGURE 3

A. Same as Figure 2*A* + 3.0 parts stearic acid
B. Same as Figure 2*B* + 3.0 parts stearic acid

Butyraldehyde aniline (Figures 4 and 5) functions in the same manner as diphenylguanidine when compounded with mercaptobenzothiazole. Since butyraldehyde aniline is a more powerful accelerator than diphenylguanidine, smaller amounts of this material were used in the accelerator mixture.

While these results indicate that some relationship exists between the two-accelerator effect and the solubility of zinc in the compound, these conclusions are, after all, largely hypothetical and can be proved only by resorting to some system which allows a separation of the zinc in solution.

EFFECT OF SOLUBLE ZINC

Bedford and Sebrell (*1*), in describing the mechanism of vulcanization, state that zinc oxide reacts with the accelerator to form the zinc salt of that compound, which in turn reacts with sulfur to form polysulfides with the zinc salt of the accelerator. The unstable polysulfides decompose, liberating sulfur available for vulcanization, along with the reformation of the zinc salt of the accelerator. Side reactions decompose and regenerate the zinc accelerator compound continually, the concentration of the zinc accelerator compound at any time being dependent upon the amount and distribution of zinc in a soluble form. Depew (*2*) determined the amount of soluble zinc formed when rubber vulcanizing agents react in a low-viscosity medium. The following method is in many respects similar to that described by Depew:

> To 150 cc. of solvent (12.5 per cent methanol and 87.5 per cent benzene) were added the compounding ingredients along with 16 cc. of the solvent saturated with hydrogen sulfide. The mixture was placed in a constant-temperature bath (46° C.) for 15 hours, after which the clear solution was filtered off and the residue thoroughly washed with portions of the solvent medium. After evaporation of the solvents the organic material was decomposed with nitric and sulfuric acids and the zinc residue titrated by a method described by Kolthoff and Pearson (*3*).

It is clear, therefore, that fatty acids improve the solution of zinc with mercaptobenzothiazole, but in the presence of diphenylguanidine they inhibit the solution of zinc. These observations are in agreement with compounding experiments which show increased ultimate tensile properties (Figure 6) when increments of stearic acid are added to 0.5 per cent mercaptobenzothiazole stock. Conversely, when 3 per cent of stearic acid is added to a stock accelerated with diphenylguanidine (Figure 7), stearic acid decidedly reduces the tensile properties of the compound.

The benzene-methanol experiments in Table II explain the series of rubber compounds shown in Figures 2 and 3. Additions of diphenylguanidine increase the amount of zinc in solution (Table II, samples 1–3), indicating that the improvement in tensile properties in the compounds (Figure 2*A*) was due to the greater amount of soluble zinc available for reaction. With additions of mercaptobenzothiazole to a constant amount of diphenylguanidine (Table II, samples 4–6) the zinc in solution remains the same, although the compounds show an increase in rate of cure (Figure 2*B*).

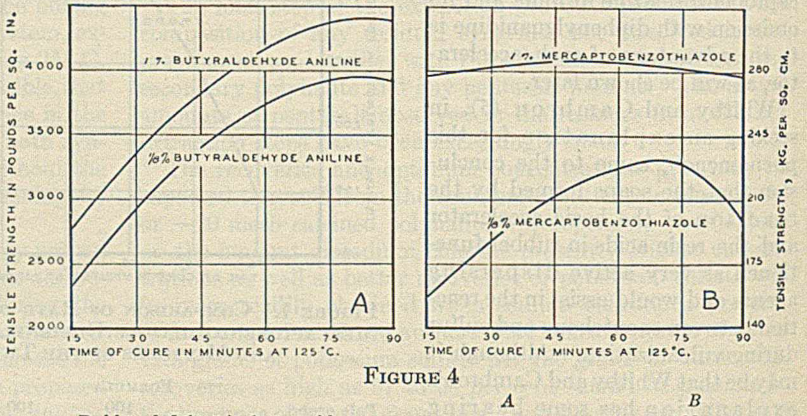

FIGURE 4

	A	B
Rubber deficient in fatty acid	100	100
Mercaptobenzothiazole	0.25	Variable
Butyraldehyde aniline	Variable	0.25
Zinc oxide	12.2	12.2
Sulfur	3.0	3.0

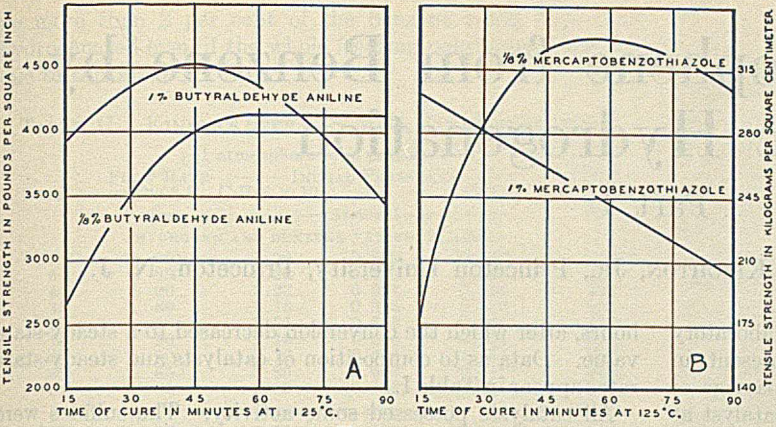

FIGURE 5

A. Same as Figure 4*A* + 3.0 parts stearic acid
B. Same as Figure 4*B* + 3.0 parts stearic acid

In the presence of fatty acids (Table II, samples 7–12) the amount of zinc in solution is reduced in all the mixtures of mercaptobenzothiazole and diphenylguanidine.

TABLE I. DATA ON BENZENE-METHANOL EXPERIMENTS

(All samples contained 5 grams U. S. P. zinc oxide and 2 grams of sulfur)

Sample	Mercapto-benzothiazole	Diphenylguanidine	Fatty Acid[a]	Zinc in Soln.
	Grams	Grams	Grams	Mg.
1	2.0	...	...	None detectable
2	2.0	...	0.3	1.6
3	2.0	...	0.6	8.1
4	...	2.0	...	19.5
5	...	2.0	0.3	9.1
6	...	2.0	0.6	8.6

[a] Coconut oil fatty acids.

TABLE II. DATA ON BENZENE-METHANOL EXPERIMENTS

(All samples contained 5 grams U. S. P. zinc oxide and 2 grams sulfur)

Sample	Mercapto-benzothiazole	Diphenylguanidine	Fatty Acid	Zinc in Soln.
	Grams	Grams	Gram	Mg.
1	1.0	0.5	...	6.2
2	1.0	1.0	...	9.2
3	1.0	2.0	...	16.8
4	0.5	1.0	...	8.7
5	1.0	1.0	...	9.4
6	2.0	1.0	...	9.3
7	1.0	0.5	0.3	1.2
8	1.0	1.0	0.3	4.5
9	1.0	2.0	0.3	13.6
10	0.5	1.0	0.3	4.7
11	1.0	1.0	0.3	4.9
12	2.0	1.0	0.3	4.0

Depew (*2*) has suggested that an equilibrium exists between mercaptobenzothiazole, its zinc compound, fatty acid, and zinc soap, and has presented evidence to show that an increase in concentration of soluble zinc increases rate of cure. A cursory examination of the data in Figure 6 would indicate a violation of the mass action principle. However, a more detailed study of the following generally accepted rubber reaction will serve to show that the present data do not conflict with that principle:

$$\text{ZnO} + \text{fatty acid} \longrightarrow \text{zinc soap} + \text{H}_2\text{O} \quad (1)$$

$$\text{Zn zoap} + \text{mercaptobenzothiazole} \rightleftharpoons \text{zinc mercaptobenzothiazole} + \text{fatty acid} \quad (2)$$

Depew selected a compound with just sufficient zinc oxide to react with all the fatty acid so that further addition of fatty acid tended to displace the equilibrium to the left (reaction 2), resulting in a retardation in rate of cure. The compounds in Figure 6 had a definite excess of zinc oxide present so that the equilibrium reaction (2) was not disturbed by addition of fatty acid. In this case, the formation of additional zinc soap (reaction 1) balances the increased concentration of fatty acid in the equilibrium reaction (2). The benzene-methanol experimental data reported in Tables I and II are not comparable to those published by Depew (*2*) since these tests were run in the presence of hydrogen sulfide which more nearly simulates rubber vulcanization conditions. Bedford and Sebrell (*1*) state that hydrogen sulfide is formed during vulcanization by the action of sulfur on the non-rubber constituents of crude rubber.

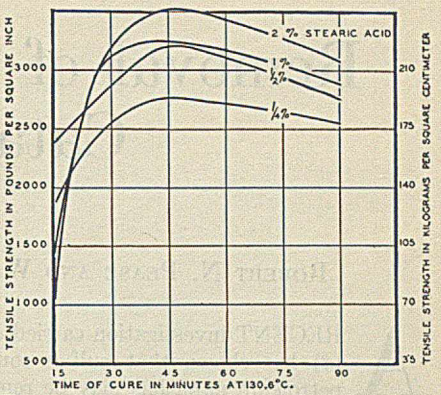

FIGURE 6. INFLUENCE OF STEARIC ACID ON A STOCK ACCELERATED WITH MERCAPTOBENZOTHIAZOLE

Rubber deficient in fatty acid	100
Stearic acid	Variable
Mercaptobenzothiazole	0.5
Zinc oxide	12.2
Sulfur	3.0

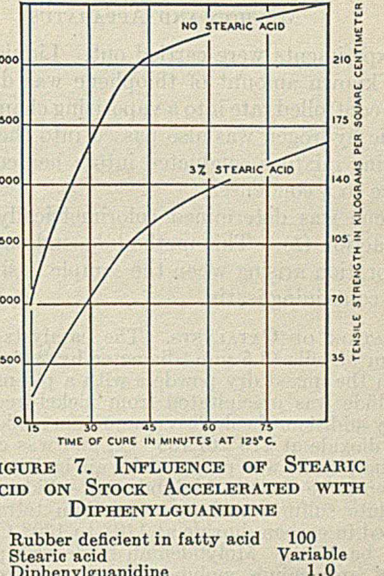

FIGURE 7. INFLUENCE OF STEARIC ACID ON STOCK ACCELERATED WITH DIPHENYLGUANIDINE

Rubber deficient in fatty acid	100
Stearic acid	Variable
Diphenylguanidine	1.0
Zinc oxide	12.2
Sulfur	3.0

LITERATURE CITED

(1) Bedford and Sebrell, J. IND. ENG. CHEM., 14, 25 (1922).
(2) Depew, H. A., *Ibid.*, 24, 565 (1932).
(3) Kolthoff and Pearson, *Ibid.*, Anal. Ed., 4, 147 (1932).
(4) Sebrell and Vogt, IND. ENG. CHEM., 16, 792 (1924).
(5) Whitby, G. S., and Cambron, A., *J. Soc. Chem. Ind.*, 42, 333T (1923).

RECEIVED March 30, 1933. Presented before the Division of Rubber Chemistry at the 85th Meeting of the American Chemical Society, Washington, D. C., March 26 to 31, 1933.

Removal of Thiophene from Benzene by Catalytic Hydrogenation

Part I

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A RECENT investigation carried out in this laboratory (*2*) has shown that sulfur compounds present in petroleum naphthas may be removed by passage of the vapor admixed with hydrogen over a nickel catalyst at 300° to 400° C. Of the sulfur compounds studied, thiophene proved the most resistant. This substance was therefore made the object of a further attack on the problem. Benzene was substituted for petroleum naphtha as a carrier for better definition, and because thiophene is a common and difficultly removable impurity in benzene.

In canvassing the possibilites as to a better catalyst than nickel, attention was called to statements in the patent literature that metal sulfides are effective (*3*), especially when admixed with metals or oxides. One of the most promising leads appeared to be systems of molybdenum and cobalt compounds. Accordingly several such catalysts were prepared and tested. The best of these (cobalt sulfide–molybdenum oxide) was then investigated in more detail.

METHOD AND APPARATUS

Flow experiments were carried out. Liquid benzene containing a known amount of thiophene was dropped from a buret at a controlled rate into a vaporizing chamber. Purified electrolytic hydrogen was also passed into the chamber, and the resulting mixture conducted into a heated catalyst tube and thence to a condenser.

Thiophene was determined colorimetrically by the indophenin reaction (*1*). This method depends upon the red-to-violet coloration arising when the sample is shaken with sulfuric acid containing isatin.

PREPARATION OF CATALYSTS. The catalysts were prepared in the form of pills (6.5 mm. diameter by 2.5 to 3 mm. thick) made from the mixed dry powders with a pill-making machine. Cobalt sulfide was precipitated from nickel-free cobalt nitrate solution by addition of colorless ammonium sulfide; it was dried in carbon dioxide at 110° to 130° C., and was considered to be CoS. Cobalt oxide was prepared by air ignition of the nitrate; it was taken to be Co_3O_4. Molybdenum sulfide was prepared by adding dilute sulfuric acid to ammonium tetrathiomolybdate. It was dried in carbon dioxide at 110° to 130° C., and was considered to be MoS_3. Molybdenum oxide was prepared by air ignition of ammonium molybdate; it was considered to be MoO_3. Kieselguhr (SiO_2) was used as an inert diluent.

All catalysts were treated with hydrogen before use, the temperature being gradually raised to 400° C. This should have left cobalt sulfide unchanged, reduced cobalt oxide largely to the metal, reduced molybdenum trisulfide to the disulfide, and molybdenum trioxide to the dioxide.

It was found that the cobalt metal catalysts reacted energetically with benzene at 400° C., freeing carbon which completely clogged the catalyst tube. As it seemed possible that the sulfur compound present would poison the catalyst for this reaction if a somewhat lower initial temperature was used, the benzene-thiophene-hydrogen mixture was first passed over at 250° C. for some hours. On raising the temperature to 400°, decomposition no longer occurred.

DISCUSSION OF RESULTS

A series of experiments was carried out with 25 cc. apparent volume of catalyst pellets and a total flow rate of 100 cc. per minute (normal temperature and pressure). In general, all thiophene was removed for a period of several hours, after which the conversion decreased to a steady-state value. Data as to composition of catalysts and steady-state rates appear in Table I.

All catalysts possessed some activity. The sulfides were preferable to molybdenum oxide or metallic cobalt, but the best catalyst was the equimolecular mixture of cobalt sulfide and molybdenum oxide (IIb). Catalyst IIa, containing much more cobalt sulfide than IIb but with kieselguhr substituted for molybdenum oxide, was definitely less active. This is a case of co-activation. The presence of metallic cobalt seems to lower the activity of molybdenum sulfide (Ia and Ib) but this may be due to carbonization of benzene induced by the cobalt. The metallic cobalt catalyst (Ic) is the least active of the lot.

TABLE I. COMPOSITION AND EFFICIENCY OF CATALYSTS

(25 cc. apparent volume catalyst pellets; total flow rate, 100 cc. per minute (N. T. P.); ratio of thiophene to benzene to hydrogen, 0.005 to 1.0 to 4.0)

CATALYST	COMPOSITION[a] Substance			THIOPHENE REMOVED (STEADY STATE) 325° C.	400° C.
		Grams	*Millimoles*	%	%
Ia	MoS_3	15.3	80	..	59
	SiO_2[b]	2.7	45		
Ib	MoS_3	13.1	68	18	34
	Co_3O_4	16.3	68		
Ic	SiO_2[b]	4.1	68	11	19
	Co_3O_4	28.5	118		
IIa	CoS	22.3	245	59	73
	SiO_2[b]	1.9	32		
IIb	CoS	4.0	44	98	100
	MoO_3	6.0	42		
IIc	SiO_2[b]	4.7	78	..	46
	MoO_3	19.6	136		
IId	MoO_3	41.6	289	21	49

[a] As made up dry per 25 cc.

[b] Kieselguhr.

KINETICS OVER CoS–MoO_3 CATALYST. Catalyst IIb was tested at 200° C. over a range of conditions. In the first series the flow rate was varied; in the second, the thiophene concentration was varied at constant benzene and hydrogen concentrations; and in the third series the benzene-hydrogen ratio was varied. Results are presented in Table II. Each series was run off as a unit and includes a "bracket." Thus, in series B, experiments 1 and 8 run under the same conditions gave 49 per cent thiophene decomposed. Variation occurred between series, however.

Series F indicates that the rate of removal of thiophene is nearly independent of the benzene (and nitrogen) concentration and is affected only to a minor degree by changes in the hydrogen concentration. Series G shows that the percentage removal of thiophene definitely decreases as the thiophene concentration is increased. The order of reaction is thus less than the first. Examination of the data obtained with varying flow rate (series B) leads to the same conclusion. This may mean either that reaction is conditioned by a nearly saturated surface layer of thiophene, or that a product (e. g., hydrogen sulfide) acts as a poison.

The possibility that the benzene is simultaneously hydrogenated was investigated by determining the freezing point before and after treatment. Any hexahydrobenzene formed would have depressed the latter (*4*). The results proved that no more than 2 per cent of the benzene could have been hydrogenated even if the whole freezing point depression was due to this alone.

TABLE II. KINETICS OVER CoS–MoO_3 CATALYST AT 200° C.

(1 atmosphere total pressure)

Expt.	Flow Rate at 200° C.	Initial Pressure: $C_4H_4S \times 10^3$	Initial Pressure: H_2	Initial Pressure: C_6H_6	C_4H_4S Reacted
	Cc./min.	Atmospheres	Atmospheres	Atmospheres	%
		HYDROGEN AND BENZENE VARIED, N_2 ADDED			
F7	90	3.32	0.322	0.678	21
6	89	3.29	0.328	0.672	23
4[a]	90	3.23	0.321	0.359	24
3[b]	89	3.15	0.325	0.350	24
5	90	3.21	0.643	0.357	33
1	90	3.19	0.646	0.354	33
2	90	3.19	0.646	0.354	35
8	85	2.86	0.683	0.317	33
9	85	2.86	0.683	0.317	31
		THIOPHENE VARIED			
G5	87	1.67	0.659	0.341	66
6	88	1.67	0.659	0.341	70
7	81	2.78	0.712	0.288	52
4	85	3.07	0.682	0.318	50
1	88	3.28	0.660	0.340	46
2	86	6.70	0.672	0.328	38
3	87	6.70	0.668	0.332	39
		FLOW RATE VARIED			
B5	370	1.84	0.625	0.375	17
6	336	1.52	0.690	0.310	23
3	195	1.97	0.596	0.404	34
4	179	1.75	0.642	0.358	34
8	94	1.89	0.614	0.386	49
1	92	1.80	0.633	0.367	49
7	89	1.71	0.650	0.350	53
2	47	1.89	0.610	0.390	74

[a] N_2 = 0.320 atm.
[b] N_2 = 0.325 atm.

ACKNOWLEDGMENT

The authors wish to express their thanks to Hugh S. Taylor who suggested this investigation.

SUMMARY

A series of catalysts, including cobalt and molybdenum sulfides, has been tested in the removal of small quantities of thiophene from benzene by hydrogenation.

An equimolecular mixture of cobalt sulfide and molybdenum oxide was the most active catalyst of those tested. At a space velocity (hours^{-1}) of 240, 0.5 mole per cent of thiophene was completely removed at 325° C., with a $4H_2{:}1C_6H_6$ mixture.

Detailed investigation of the reaction at 200° C. in the presence of the cobalt sulfide–molybdenum oxide catalyst showed that the rate was little affected by changes in hydrogen or benzene concentrations. The order with respect to thiophene was less than the first, indicating either a nearly saturated surface layer of thiophene, or poisoning by-products.

LITERATURE CITED

(1) Allen, "Commercial Organic Analysis," 5th ed., p. 517, Blakiston, 1926.
(2) Elgin, J. C., Wilder, G. H., and Taylor, H. S., IND. ENG. CHEM., 22, 1284 (1930); Elgin, *Ibid.*, 22, 1290 (1930).
(3) I. G. Farbenindustrie, British Patent 315,439 (May 24, 1928).
(4) Mascarelli and Pestalozza, *Atti accad. Lincei*, [2] 16, 574 (1907).

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Part II

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IN EXTENSION of the investigation reported in Part I, additional catalysts have been tested. The method and apparatus used are unchanged.

Four catalysts were prepared as follows:

1. Cobalt oxide from the nitrate was reduced in hydrogen and subsequently treated with hydrogen sulfide gas to produce a surface layer of sulfide.
2. Cobalt sulfide and chromic oxide were co-precipitated from their nitrate solutions with ammonium hydroxide and hydrogen sulfide. The ratio was one mole CoS to one mole Cr_2O_3.
3. Chromic oxide was precipitated from the nitrate with ammonium hydroxide. This catalyst retained much water at 110° to 130° C.
4. Cobalt oxide and molybdenum sulfide were mixed in powder form. The ratio was one mole Co_3O_4 to one mole MoS_3.

All catalysts were made into pills of which 25 cc. apparent volume were used. All samples were first treated with hydrogen at 400° C. and then with the hydrogen-benzene-thiophene mixture also at 400°. Tests were made with a mixture of 1 mole benzene, containing 0.5 mole per cent thiophene, to 4 moles hydrogen. The total flow rate was 100 cc. per minute (normal temperature and pressure). Results for steady-state operation are given in Table I.

TABLE I. EFFICIENCY OF CATALYSTS

Catalyst	Description	Thiophene Removed 200° C.	Thiophene Removed 400° C.
		%	%
1	Cobalt treated H_2S	0	1
2	CoS–Cr_2O_3	38	100
3	$Cr_2O_3.xH_2O$	0	100
4	Co–MoS_2	37	98

Comparison of these results with those of Keighton (Part I) indicates that catalysts 2 and 4 were as good as Keighton's best catalyst IIb (CoS–MoO_3). Catalyst 4 was much superior to the corresponding preparation made by Keighton. The reason for this is not clear, since the only difference was that, after reduction, Keighton's preparation was treated with the reaction mixture first at 200° C. while Munro's preparation was first treated at 400°. The treatment at 200° was intended to prevent carbonization.

The inactivity of catalyst 1 was unexpected. Pure cobalt was found by Keighton to have moderate activity, whereas cobalt sulfide was next to the best catalyst. It might have been expected that a surface layer of sulfide on cobalt would lie between, instead of being the least active. The explanation is presumably to be sought in the existence of an unbroken layer of sulfur on the cobalt treated with hydrogen sulfide. Such a layer is probably firmly bound as compared to a similar layer on the fully saturated sulfide. Hence, interchange with the substrate would be more difficult. Presumably if the untreated metallic cobalt was exposed to the reaction mixture under such conditions that most of the sulfur remained on the surface, similar inactivity would have resulted. The fact that the hydrogen has access to the sulfur while it is being laid down gives the untreated cobalt catalyst such activity as it possesses.

SUMMARY

Cobalt sulfide plus chromium oxide, and chromium oxide alone are good catalysts for removal of thiophene from benzene by hydrogenation.

Metallic cobalt pretreated with hydrogen sulfide is inactive, although untreated cobalt and cobalt sulfide are active.

RECEIVED February 27, 1933. This paper contains results of an investigation carried out as part of Project 40 of American Petroleum Institute research. Financial assistance has been received from a research fund donated by John D. Rockefeller. This fund was administered by the American Petroleum Institute with the coöperation of the Central Petroleum Committee of the National Research Council. Hugh S. Taylor of Princeton University was director of Project 40.

Rate of Solution of Methane in Quiescent Liquid Hydrocarbons

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An apparatus has been constructed which allows the determination of diffusion constants and solubilities of gases in liquids at pressures up to 30 atmospheres. The possibilities and limitations of the method have been investigated both theoretically and experimentally. Results obtained with methane dissolving in isopentane are found to be in good agreement with theoretical equations. A consideration of the assumptions involved, together with the consistency of the results, indicates that the method is capable of giving fairly reliable values for the true absolute diffusion constant, although the probable error may be as great as 4 per cent. An investigation of the extent to which the diffusion constant may be affected by pressure or by the concentration of methane gas in solution up to pressures of 20 atmospheres (approximately 300 pounds per square inch) did not reveal any effect.

INCREASING use in recent years by the petroleum industry of the process of "repressuring" by forcing gases into an oil formation has led to a desire for more intimate knowledge of the nature of the changes taking place during this process. It is desirable to know, among other things, the extent to which gas will dissolve and diffuse into the oil in a formation.

Some measurements are on record of the rate of diffusion of a few gases in water and aqueous solutions and in alcohol (*4*). However, no information has been found which will furnish a reliable basis for predictions as to the extent to which gases will diffuse through oils and oil sands, especially at high pressure.

For practical purposes it is most important to know how gases diffuse through oil sands, but the initial experiments treated the simpler cases of homogeneous liquids. In this article some theoretical considerations are discussed, and the apparatus which has been evolved for making the desired measurements is described. Only such experimental data are presented as are needed to demonstrate the method and the principles involved.

Theoretical Part

The mechanism of the diffusion of various solutes through aqueous solutions was considered first by Parrot in 1815. Graham (*2*) made the first real investigation of the subject in 1850, and Fick (*1*) later proposed that "the quantity of salt which diffuses through a given area is proportional to the difference between the concentrations of two areas infinitely near one another." Subsequent investigations have demonstrated the validity of Fick's proposition (*6*).

Assuming this proposition, we may write:

$$\frac{\delta q}{\delta t} = -DA\frac{\delta C}{\delta x} \qquad (1)$$

where q = quantity of solute which has passed a given point
A = area at right angles to direction of flow
C = concentration
x = distance in direction of flow
t = time
D = diffusion constant

If centimeter-gram-second units are used, this equation defines the absolute diffusion constant. Its dimensions are square centimeters per second.

Under experimental conditions, a gas is caused to diffuse into a body of liquid in the form of a cylinder, with the surface of the liquid perpendicular to the axis of the cylinder. It is desired to know the rate at which the gas will be absorbed by the liquid, and how the gas will distribute itself in the body of the liquid. Two cases should be considered: (1) The cylinder of liquid is of infinite length; and (2) the cylinder is of finite length.

Cylinder of Liquid of Infinite Length. In this discussion only those cases are considered in which the initial concentration is uniform and in which the pressure of gas on the surface of the liquid is kept constant during the experiment. Furthermore, it is assumed that the layer of liquid immediately under the surface is always saturated. The saturation concentration (in cc. of gas per cc. of solution) may be represented by C_s. Letting the initial concentration be C_0 and the distance below the surface of the liquid be x, these conditions may be embodied in the equations:

$$C = C_0 \text{ at } t = 0 \text{ for all values of } x \qquad (2)$$

$$C = C_s \text{ at } x = 0 \text{ for all values of } t \qquad (3)$$

The mathematical procedure for the solution of Equation 1 was first worked out by Fourier in connection with the treatment of the problem of the flow of heat, and may be found in mathematical textbooks, especially Ingersoll and Zobel (*3*). The application to the case of gas diffusion is credited to Stefan (*7*). The solution subject to the given conditions is:

$$\frac{C - C_0}{C_s - C_0} = 1 - \frac{2}{\sqrt{\pi}}\int_0^{\frac{x}{2\sqrt{Dt}}} e^{-\beta^2}\,d\beta \qquad (4)$$

In most of the experimental work, C_0 is 0, in which case the left side of the equation becomes C/C_s and represents the fraction of the saturation concentration or the degree of saturation at any point in the liquid. The integral is of the form known as the probability integral, and values for it may be found in mathematical tables. A plot of this equation (letting $C_0 = 0$) is given in Figure 1.

If one differentiates Equation 4 with respect to x, substitutes in Equation 1, lets x equal 0, and integrates, there is obtained an expression for Q, the total amount of gas which has dissolved since the beginning of the diffusion process. The equation is:

$$Q = 2C_sA\sqrt{\frac{Dt}{\pi}} \qquad (5)$$

The derivation of these equations involves certain assumptions as follows: (a) Equation 1 assumes that the diffusion constant does not change with the concentration of the solution; (b) Equation 3 assumes, in the case of a gas diffusing into a liquid, that the layer immediately under the surface is always saturated—that is, that a surface film does not retard the passage of gas into the liquid; (c) the gas moves through the liquid only by diffusion.

(a) The first assumption cannot be more than an approximation. Experiments have been made, as will be related later, in an attempt to find to what extent the rate of diffusion is influenced by the concentration.

(b) With regard to the second assumption, if there is present a surface film which retards the passage of the gas into the liquid, the retardation would be more serious in the early part of a run when the gas is diffusing away from the surface rapidly, and would have relatively less effect later in the run when the gas is diffusing more slowly. Thus the rate of solution would be slower near the beginning of a run than the rate demanded by the equations. If the form of Equation 5 were experimentally verified, it would prove that the second assumption was substantially true.

(c) The third assumption is not accurately true, even in the absence of convection currents. For when the gas dissolves in the liquid, the volume of the solution is greater than the volume of the original liquid. This expansion is of the order of 1 to 4 per cent at saturation in these experiments, with methane at pressures up to 20 atmospheres (approximately 300 pounds per square inch). A mathematical treatment of this effect has been devised, and it is found that the error which is introduced into Equation 5 is negligible in these cases. In some later experiments with methane at higher pressures, and with ethane and propane, the effect was not negligible. The magnitude of the correction will be discussed in a later article when those results are described.

Cylinder of Liquid of Finite Length. Let l be the length of the cylinder of liquid. At the end of the column of liquid there will be no flow and hence no concentration gradient. Hence Equation 1 should be solved subject to the condition:

$$\frac{\delta C}{\delta x} = 0 \text{ at } x = l \qquad (6)$$

As before, the solution may be found in mathematical works. Concentration is given by the equation:

$$\frac{C - C_0}{C_s - C_0} = 1 - \frac{4}{\pi} \sum_{m=1}^{m=\infty} \frac{1}{2m-1} e^{\frac{-D(2m-1)^2\pi^2 t}{4l^2}} \sin (2m-1)\pi x/2l \qquad (7)$$

When t is large (late in a run), all terms of the summation beyond the first can be neglected, and, for the case where C_0 is zero, there is obtained the expression:

$$\frac{C}{C_s} = 1 - \frac{\pi}{2}\left(1 - \frac{Q}{Q_s}\right) \sin \frac{\pi x}{2l} \qquad (8)$$

where Q_s = quantity of gas dissolved in liquid at saturation. This shows that the diffusion concentration curve in this case becomes a simple sine curve.

The expression for the total amount of gas which has diffused into the liquid is:

$$Q = C_s A l \left[1 - \frac{8}{\pi^2} \sum_{m=1}^{m=\infty} \frac{e^{-D\left(\frac{2m-1}{2l}\right)^2 \pi^2 t}}{(2m-1)^2} \right] \qquad (9)$$

When t is very small, so that the gas behaves as though it were diffusing into an infinite column of liquid, Equation 9 reduces to Equation 5. When that equation is compared with Equation 9, it is found, by making calculations according to both equations, that 9 differs from 5 by only 0.02 per cent when the amount of gas dissolved in the liquid is 30 per cent of the amount necessary to saturate the liquid, by 0.25 per cent when the liquid is 50 per cent saturated, and by only 4.7 per cent even when the saturation is 70 per cent.

On the other hand, as t increases, the summation in Equation 9 converges more and more rapidly, until finally it is possible to neglect all terms beyond the first, in which case there results the equation:

$$Q = C_s A l \left[1 - \frac{8}{\pi^2} e^{-Dt\left(\frac{\pi}{2l}\right)^2} \right] \qquad (10)$$

This approximation involves an error of only 0.20 per cent when the saturation is 50 per cent and decreases rapidly as the saturation increases. Hence one can fairly accurately describe the course of a diffusion run by Equation 5 from 0 to 50 per cent saturation and by Equation 10 from 50 to 100 per cent.

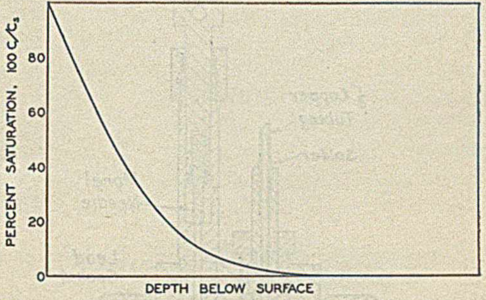

Figure 1. Characteristic Distribution of Gas Diffusing into Liquid from the Surface

In this case the expansion of the solution not only results in transporting some of the solute farther from the surface, but also causes l to have a changing value. A careful consideration of what value should be given to l, in the absence of a rigorous mathematical treatment, has indicated that if l is taken as the length of the column of saturated solution, no appreciable error will be caused by the changing length.

Materials and Apparatus

Materials. The liquids used in the experiments described were isopentane, and a high-boiling gasoline fraction. The isopentane was obtained by repeated fractionation of casinghead gasoline. The material used had a boiling range of 27.3° to 28.2° C. (corrected to 760 mm.).

In order to obtain the gasoline fraction, a quantity of commercial gasoline was fractionated three times. The portion boiling between 170° and 180° C. was given intensive treatment with fuming nitric acid, washed with sulfuric acid, water, and sodium hydroxide solution, dried over calcium chloride, and fractionated several more times. The final product had a boiling range of 79.4° to 88.5° C. at 38 mm.; density at 30° C. = 0.7894 gram per cc.; index of refraction at 23° C. for sodium D line = 1.4399. A consideration of these properties indicates that the material probably consisted largely of naphthenes.

The gas used was methane, obtained from dry natural gas from Southern California fields. The samples of natural gas used contained between 85 and 95 per cent of methane. The methane was purified by allowing it to stand for a half-hour or more at a pressure of 35 to 70 atmospheres (500 to 1000 pounds per square inch) in a cell filled with activated charcoal. The methane obtained by this method was analyzed occasionally by passing a known volume into a liquid-air trap and then applying a vacuum to the trap for a suitable length of time. All of the probable constituents of the gas except methane and nitrogen are completely retained in such a trap, and may be measured by the pressure which they exert after removing the liquid air. The condensable fraction, doubtless consisting principally of ethane, was never found to be over 2 per cent, and was usually about 1.5 per cent. The gas from

Southern California fields is known to contain very little nitrogen. Furthermore, the nitrogen, by virtue of having a solubility less than that of methane, would in part counteract the effect of the ethane, which has a greater solubility.

APPARATUS. The plan adopted for the determination of diffusion rates was to place the liquid in a cylindrical cell, admit gas to the cell until the desired pressure was reached, and then keep this pressure as nearly constant as practicable by adding more gas from time to time to replace that which diffused into the liquid. The volume of gas which had been added was determined, and this, together with the times corresponding to the additions, constituted the data for the calculation of diffusion constants.

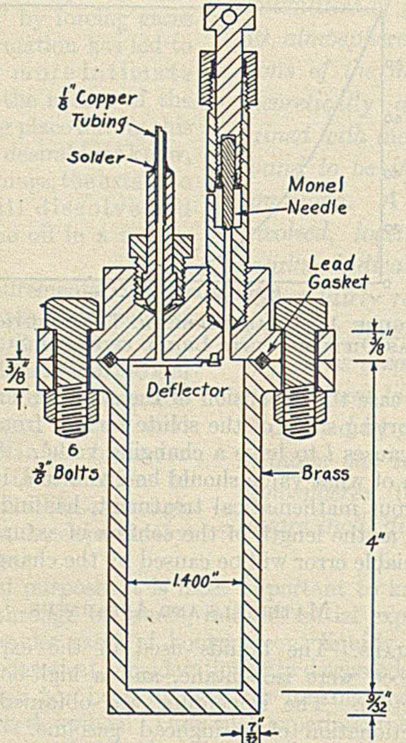

FIGURE 2. ABSORPTION CELL

Figure 2 shows diagrammatically the apparatus now being used for the making of these measurements. The apparatus was remodeled recently, and hence the one used for the measurements described in this article was not identical with that shown in the diagram, but the changes did not involve any new principles.

The absorption cell is made of brass with walls 5.5 mm. thick, and has an inside diameter of 35.54 mm. and an inside length of 102 mm. The cell is closed by a brass plate which bolts on to a flange around the top of the cell. Into the plate and the flange are cut matched grooves 2.4 mm. deep. A lead gasket is cast to fit these grooves and serves to make the cell gas-tight in a very satisfactory manner. The top plate is fitted with an outlet valve and a connection to flexible copper tubing through which the gas is admitted to the cell. A 3.5-inch (8.9-cm.) 500-pound, Crosby test gage, connected to the copper tubing, serves to measure the pressure in the cell. This test gage is calibrated from time to time against a dead-weight tester. A copper shield in front of the inlet prevents the incoming gas from causing agitation of the surface of the liquid.

The valve controlling admission of gas to the cell is sensitive enough to allow the gas to be admitted a fraction of a cubic centimeter at a time if necessary, even with a differential pressure of several hundred pounds. The packing on the low-pressure side must be practically leak-proof. Leakage of one cc. a day is the maximum that could be tolerated. Raw-hide disks were previously used, but these have been replaced by metallic packing moistened on the inside with a very small amount of mercury. This same packing arrangement is being used on an apparatus operating at 170 atmospheres (2500 pounds per square inch) and shows no detectable leakage.

During the experiments described, the reservoir from which gas was admitted to the cell consisted of an 8-inch (20.3-cm.) Ashton bronze-tube gage, reading from 300 to 600 pounds per square inch (approximately 20 to 40 atmospheres). In order that the readings of the gage might be used as a measure of the amount of gas in the reservoir, calibrations were carried out by filling the gage with gas and withdrawing it, by steps, in a very accurate pipet at atmospheric pressure, the corresponding gage pressures being recorded. From these data, charts were prepared giving the total amount of gas delivered when the gage dropped from its maximum reading down to any other reading.

The volume of this gage was a little over 100 cc. Readings were made to 1/6 pound, corresponding to about 1.2 cc. In spite of the fact that the gage was only of the ordinary type intended for industrial use, remarkably good results were obtained. Two calibrations made a week apart, covering a range of 1000 cc., gave curves deviating from each other irregularly by an average of 1.9 cc. with no definite trend to the deviations. Other duplicate calibrations gave similar results of at least equal reproducibility. The gage was calibrated every 2 to 4 months. Over these intervals of time, some definite change was always noted, sometimes in the direction of larger volumes, sometimes of smaller. The maximum difference was about 5 per cent, with the difference between successive calibrations never exceeding 2 per cent. Interpolations between successive calibrations were made on the basis of the time interval.

The apparatus thus far described was enclosed in an air bath controlled by a thermostat. This thermostat maintained the temperature within 0.05° C. of the desired value.

The increase in volume of the liquid when the gas is dissolved in it must be known for the correct interpretation of the results. This was obtained in an apparatus similar in principle to one used by Mills and Heithecker (*5*) but constructed of glass. Two glass bulbs, a lower one of 25 cc. volume and an upper one of 15 cc. were joined by a graduated tube 0.472 cm. in diameter and 13 cm. in length. An outlet from the upper bulb led to one side and downward, and to this was fastened a high-pressure rubber hose, which communicated with a gage and with the supply of methane.

By filling this apparatus with oil up to a mark in the graduated tube, evacuating, and then saturating with gas under pressure by repeatedly inverting the apparatus, and noting the rise in the height of the oil, the increase of volume could be calculated. This apparatus has withstood a pressure of over 13 atmospheres (200 pounds per square inch). Readings were taken at three or more successively increasing pressures. The increase in the height of the oil at 10 atmospheres (approximately 150 pounds) was usually 2 to 4 cm. By using care to secure uniform drainage conditions, and by keeping the apparatus thoroughly thermostated, readings could be obtained which were consistent to 0.03 cm.

EXPERIMENTAL RESULTS

General Equation 9 expressed the quantity of gas dissolved in the liquid as a function of time, which should be valid throughout the entire course of an absorption run. Equations 5 and 10 were shown to be close approximations to 9, valid, respectively, for the first half and the last half of a run. The diffusion constant is most easily determined by continuing an absorption run until the liquid is not over 50 per cent saturated, and applying Equation 5. However, it seemed worth while to carry one run very near to completion and thereby subject the absorption equations to a more rigorous test. The liquid chosen for this purpose was isopentane.

The diffusion cell was partly filled with 28.69 grams of isopentane, and, after assembling the apparatus and bringing it to 30° C., methane was admitted until the gage on the cell read 200. No attempt was made to remove the air from the cell, because if the air in the gas phase is in equilibrium with air dissolved in the liquid, which we may assume is approximately the case, this equilibrium will be only slightly affected while the methane diffuses into the oil. A careful consideration of the extent to which this equilibrium would be disturbed has shown that any error due to this cause is negligible. After making necessary corrections for error in the gage and for partial pressures of air and isopentane vapor, the partial pressure of the methane in this run was found to be 192.5 pounds per square inch (13.1 atmospheres).

During the course of the run the gage was usually allowed to drop to about 198 pounds per square inch (13.5 atmospheres); gas was then admitted until the reading was 200 (13.6 atmospheres) and the time and the reading of the reservoir gage recorded. More gas was admitted until the gage read 202 (13.7 atmospheres) (or as far above 200 as it had previously fallen below 200), and the apparatus was then allowed to stand until the pressure had again fallen to 198 pounds per square inch. It has been determined experimentally that if the fluctuations of pressure are allowed to become as great as 15 pounds (one atmosphere) instead of the limit of 4 pounds (0.27 atmosphere) observed in this run, no effect upon the average course of the absorption of gas is noted. Hence it may be assumed that, when the pressure fluctuates regularly between 198 and 202 pounds, the gas diffuses substantially as though the pressure were constant at 200 pounds per square inch.

The diffusion process was continued for 82 hours, until the liquid was 98.9 per cent saturated, and then the cell was removed from the support and shaken to obtain complete saturation. Sixty sets of readings were obtained in this run.

The exact amount of gas which must be admitted to the cell in order to raise the pressure to the desired value before any gas dissolves cannot be directly determined. The gas may be admitted very rapidly up to the run pressure, and the reservoir gage read immediately, but even this reading would have no significance, for effects due to the heat of compression render invalid any readings for at least a minute. The rate of absorption at the beginning of the run is, of course, very high, and so several cubic centimeters of gas are absorbed in the first minute.

In spite of this difficulty, the total amount of gas admitted to the cell may be plotted against $\sqrt{t}$, and a straight line should result if Equation 5 is valid. Or, more conveniently, one may plot against $\sqrt{t}$ the volume equivalents of the gage readings as obtained from the calibration charts. These values differ from the actual volumes of gas admitted by some constant quantity corresponding to the reading of the reservoir gage before the start of the run. Such a plot of the data of this run is shown in Figure 3. Gas volumes are calculated for one atmosphere pressure and 30° C. It will be seen that a fairly straight line is obtained for the first part of the run, and this verifies the form of Equation 5.

TABLE II. DIFFUSION CONSTANTS FOR METHANE AT 30° C. (86° F.)

LIQUID	PRESSURE INTERVAL		m' UNCOR. SLOPE	m COR. SLOPE	C_s SOL. OF GAS PER CC. SATD. SOLN.	C_s/p SOL. PER LB./SQ. IN.	C_s FROM AV. C_s/p	$D \times 10^5$
	Atm.	*Lb./sq. in.*	*Cc./$\sqrt{hours}$*		*Cc.*			
Isopentane	0-13.10	0-192.5	82.7	85.7	10.95	..	..	14.00
Gasoline fraction	0- 9.77	0-143.5	27.0	27.7	6.00	0.0418	5.93	4.97
Gasoline fraction	9.77-19.56	143.5-287.5	26.5	27.8	5.98	0.0415	5.93	5.01
Gasoline fraction	0-19.56	0-287.5	53.1	55.5	11.77	0.0409	11.87	4.98

If this straight line is extrapolated to zero time, a value of 374.5 cc. is obtained. When this number is subtracted from the volume equivalents of the gage readings, values are obtained which correspond to the volume of gas admitted after what may be considered the start of the diffusion process. In other words, 374.5 cc. is the equivalent of the reservoir reading which would be obtained if the cell were filled just to a pressure of 13.1 atmospheres (192.5 pounds per square inch) of methane but without any gas diffusing into the oil.

The values obtained by subtracting 374.5 from the subsequent readings are not the volumes of gas actually dissolved by the oil, a correction being necessary because of the expansion of the liquid when the gas dissolves in it and the consequent reduction in the volume of the gas space. It can easily be shown that the correction factor which must be applied to the volumes of gas admitted to the cell in order to give the volumes dissolved is $1/(1 - \epsilon p)$, where ϵ is the increase in volume of the solution per cc. of gas dissolved, and p is the pressure in atmospheres. Values for ϵ were found by use of the change-of-volume apparatus described previously. A summary of the data used for these calculations is given in Table I. The values for the volume of gas dissolved are calculated from solubility coefficients obtained from saturation values of the absorption runs, after first making preliminary corrections of these saturation values with approximate values of ϵ.

TABLE I. EFFECT OF DISSOLVED METHANE UPON VOLUME OF LIQUID AT 30° C. (86° F.)

LIQUID	PRESSURE INTERVAL		INCREASE IN VOL.	GAS DISSOLVED[a]	INCREASE OF VOLUME PER CC. GAS DISSOLVED
	Atm.	*Lb./sq. in.*	*Cc.*	*Cc.*	*Cc.*
Isopentane (26.53 cc.)	0- 2.89	0- 42.5	0.172	65.6	0.00262
	0- 6.29	0- 92.5	0.392	142.8	0.00274
	0- 8.62	0-126.7	0.531	195.6	0.00271
	0-10.06	0-147.8	0.614	228.0	0.00269
		Weighted average			0.00270
Gasoline fraction (33.89 cc.)	1.44-6.76	21.1- 99.4	0.240	110	0.00218
	1.44-8.30	21.1-122.0	0.309	142	0.00218
		Weighted average			0.00218

[a] At one atmosphere pressure and 30° C.

The consistency of the results obtained indicates that the accuracy is more than adequate for making the small expansion correction with a considerable degree of certainty. There is no evidence of a variation of ϵ with the pressure, so that the use of these values at somewhat higher pressures is justifiable. Furthermore, results of Mills and Heithecker (5) obtained with dry natural gases and crude oils indicate that ϵ is constant up to 1000 pounds per square inch (68 atmospheres).

The correction factor for this run is 1.0367; when this factor is applied, the volume of methane dissolved at saturation is 524 cc. (at one atmosphere and 30° C.). The height of the liquid at saturation (l of Equation 10) is calculated to be 4.898 cm. The volume of the liquid at saturation is calculated to be 47.87 cc., corresponding to a cross-sectional area, A, of 9.774 sq. cm. Dividing 524 cc. by 47.87 cc. gives 10.95 cc. of gas per cc. of saturated solution as the value of C_s.

The diffusion constant may be calculated from the equation

$$D = \frac{\pi m^2}{14{,}400\, A^2 C_s^2}$$

obtained by differentiating Equation 5 and converting hours to seconds. Values for the diffusion constant, D, were calculated for each set of readings, using Equation 5 or 10 as required. The average value is 14.00×10^{-5} sq. cm. per second. As a test of the accuracy with which the data fit the equations, this average value of D was used to calculate the volume of gas which should have been absorbed at the time of each reading. These calculated values differ from the experimental values by an average of 1.5 cc. At only six of the sixty points does the deviation exceed 3 cc. with a maximum deviation of 4.2 cc. This is well within the limits of error of the method of measurement. There is no definite trend to the deviations.

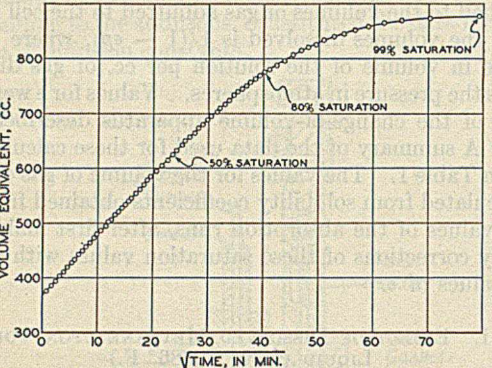

Figure 3. Absorption Rate Data at 30° C. (86° F.) for Methane in Isopentane

Ordinarily the absolute diffusion constant may be conveniently calculated from the slope of the line obtained when volumes are plotted against square roots of time, rather than from the data of individual points. Furthermore, it is not necessary to apply the correction factor for expansion of the liquid to the volumes before plotting; we may merely correct the slope of the line obtained by plotting the original volume equivalents of the reservoir gage readings. The uncorrected slope of the line as obtained from a large-scale plot of the volume equivalents against the square root of the time in hours is designated as m'. When the correction factor is applied to m' the corrected slope, m, is obtained.

The bearing of these results upon certain assumptions which are inherent in the calculations may be examined:

(1) It has been assumed that the rate of diffusion is independent of the concentration. The proportionality between Q and $\sqrt{t}$ involved in Equation 5 early in a run would be obtained regardless of any effect that the solute might have on the properties of the solvent. In fact, it can be shown that the only requirement necessary to obtain this relationship is that the curve representing the distribution of solute under the surface should always have the same shape, regardless of what it might be, merely expanding in the x direction with increasing time. However, if the rate of diffusion is influenced to a considerable extent by the dissolved gas, a changing value of D should be observed during a run which is carried near to saturation. The constancy of the values of D found in the isopentane experiment would seem to indicate that the concentration did not have any very great effect upon D, although a small effect might escape notice.

(2) Saturation of the surface layer at all times is assumed. As was pointed out previously, an increasing value of D would be obtained if the liquid immediately under the surface were not completely saturated at all times. The experimental results seem to be good evidence that there is no appreciable retardation, under these experimental conditions, in the passage of the gas through the surface of the liquid.

(3) It is assumed that no solute is transferred by convection. The tendency for convection to take place is greatly reduced by the fact that the solutions of methane in oils have a lower density than the pure oils. The difference in density in this isopentane experiment is calculated to be 2.7 per cent. By virtue of this fact, a stable density gradient is established. One of the preliminary experiments was made with carbon dioxide and kerosene. It gave a very high diffusion constant at first, decreasing greatly with time. The explanation of this is that the solution is heavier than the pure liquid, and hence convection occurs, this effect being most pronounced when there is only a little gas in solution. Tests to indicate how great fluctuations in temperature would be necessary to introduce convection errors showed that the accuracy of thermostating was adequate. The fact that the experiment agrees so well with the theoretical equations is an indication that there were no appreciable convection effects.

In order to obtain more information as to the effect of the concentration upon the diffusion rate, a so-called split run was tried with the high gasoline fraction. In this experiment a diffusion run was made at 143.5 pounds per square inch (9.76 atmospheres) pressure, the liquid was then saturated at that pressure, and another diffusion run was made upon the resulting solution at 287.5 pounds per square inch (19.56 atmospheres), or almost exactly twice the first pressure. Another experiment was then made in which the pressure was raised at once from 0 to 287.5 pounds. If the diffusion constant is not appreciably affected by the concentration, and if the solubility is proportional to the pressure, the rate of solution should be the same in the first two cases, and twice as great in the third.

In Figure 4 these runs are shown graphically; in Table II is given a summary of the results. C_s for the second half of the split run refers just to the gas dissolved above 9.76 atmospheres (143.5 pounds per square inch). When the values of C_s are divided by the pressure intervals (in pounds per square inch) the values obtained are approximately constant, the difference being within the limits of experimental error. A weighted average of this ratio of C_s/P is used to calculate values of C_s for substitution in Equation 5. In view of the fact that D depends upon the square of m, the three values are seen to agree surprisingly closely; actually the expected experimental error is considerably greater than the differences which appear in the results.

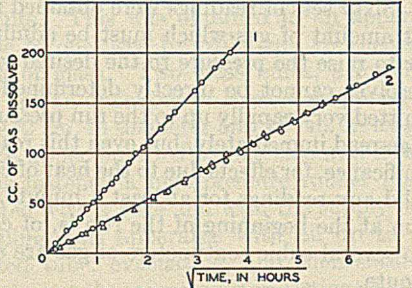

Figure 4. Absorption Rate Data at 30° C. (86° F.) for Methane in Gasoline Fraction (45.4° A. P. I.)

Curve 1. Pressure changed from 0 to 19.56 atmospheres

Curve 2. ⊙ Pressure changed from 0 to 9.76 atmospheres

△ Pressure changed from 9.76 to 19.56 atmospheres

From a consideration of the information furnished by the experiments which have been described and from a consideration of the probable experimental errors, it seems safe to say that any effect which the concentration or pressure up to 20 atmospheres (approximately 300 pounds per square inch) may have upon the rate of diffusion of methane in light oils probably does not exceed 4 per cent.

In addition to the possible sources of error which have been discussed, there was another present in these experiments which probably was not negligible—the effect of the impurities in the methane. Since ethane is more soluble in oils than is methane, a content of 1 to 2 per cent of ethane might be expected to give a rate of solution slightly higher (not over one per cent) than would be obtained with pure methane.

However, the preparation of an adequate supply, under pressure, of methane of higher purity than that which was used is a difficult undertaking, and it seemed probable that the slightly impure methane would give results accurate enough for the purpose for which the experiments were originally undertaken.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Fick, *Pogg. Ann.*, 94, 59 (1855).
(2) Graham, *Phil. Trans.*, 1850, 1, 850; 1851, 483.
(3) Ingersoll and Zobel, "Mathematical Theory of Heat Conduction," Ginn, 1913.
(4) International Critical Tables, Vol. V, p. 63, McGraw-Hill, 1929.
(5) Mills and Heithecker, Bur. Mines, *Rept. Investigations* 2893 (1928).
(6) Ostwald, W., "Solutions," tr. by Muir, M. M. P., pp. 118–55, Longmans, 1891.
(7) Stefan, *Sitzber. Wien Akad.*, 79, Abt. II, 177 (1879).

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Chemical Treatment of Rotary Drilling Fluids

Stabilization of Weighted Dispersions: Effect of pH Value

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Weighted rotary drilling fluids are discussed from the standpoint of colloid physics, with emphasis on the stability of dispersions of barytes as a function of the pH of the dispersion medium. It is shown why a material such as bentonite is superior to chemicals as the protective colloid, and how the stability of the commercial product Baroid changes with the pH of the suspending medium. The curve obtained for the amount of Baroid remaining in suspension in a 25 per cent dispersion in water as a function of pH shows two maxima, one on the acid side and one of greater magnitude on the alkaline side, with the isoelectric point at pH = 8.7. There is an enormous increase in the stability of the suspension when the pH is increased from the range 8–10 to the range 10.5–11.5—i. e., an increase from 25 to practically 100 per cent remaining in suspension in 12 hours. The results are applied to actual drilling practice.

THERE are two standardized methods now in general use for boring oil wells, the cable tool or "standard rig" and the hydraulic rotary system of drilling. In cable tool drilling the bit is caused to rise and fall by a suitable mechanism, alternately withdrawing and releasing the suspending cable, thus pounding and fracturing the rock formations beneath the bit. The rock cuttings are suspended by a short column of water in order to expose constantly a fresh surface to the bit. The accumulation of such material would soon cause inefficient drilling, of course, and therefore the bit is frequently withdrawn to permit the removal of accumulated debris by means of a bailer. It is clear that the downward velocity of the drilling tool would be greatly diminished if the column of suspending medium were too high, resulting in slow and inefficient drilling. For this reason it is necessary to case off water horizons; and, inasmuch as each water horizon encountered requires a separate string of casing, an excessive number of strings of casing may be needed. This practice results in excessive cost for casing, together with rapid tapering of the bore hole and necessarily the use of smaller size bits as drilling proceeds.

The hydraulic rotary method consists of rotating a column of hollow drill pipe with a drilling tool attached to its extremity. During the operation of cutting away the rock mass as a result of the downward pressure of the rotating bit, drilling fluid is circulated down the hollow drill stem by means of powerful pumps. The rock cuttings, which are flushed away from the face of the cutting tool by the flow of the drilling fluid through orifices at the bit face, are carried to the surface by the fluid returning through the annular space between the drill stem and well bore. Fewer strings of casing are required with the hydraulic rotary method of drilling than with the cable tool method, for water and gas formations are sealed off by the hydrostatic head of the fluid column, this sealing action serving the purpose of casing, to a certain extent. An important function of the drilling fluid is the prevention of caving of loose and unconsolidated formations; hence, the rotary system of drilling has been employed for many years for drilling through soft and caving horizons. The recent development of hard-rock cutting bits and bits with hard-faced cutters has resulted in the rotary displacing cable tools for very deep drilling in the harder formations, with certain exceptions, and it is probable that the former method will be used almost exclusively in the future for deep wells. The advantages of the rotary system are greater speed in drilling, decreased cost for casing, the control of water and gas formations, and prevention of dangerous blow-outs of oil and high-pressure gas. The modern core barrel and drill stem tester have eliminated the chief disadvantage of the rotary system, which is the possibility of sealing off valuable oil formations, without the driller knowing that such horizons have been found.

DRILLING FLUIDS

It has now become generally recognized that the proper quality and control of the drilling fluid used in the hydraulic rotary method is of paramount importance. Drilling fluid has three main functions:

(1) It removes rock cuttings from around the bit and carries

them to the surface, where the larger particles are either settled out in a pit or removed by special mechanical devices.

(2) The hydrostatic head of the fluid column seals off water, gas, and minor oil-bearing formations. This head is controlled by proper adjustment of the density of the fluid, using so-called weighting materials of high density when clay suspensions are no longer adequate.

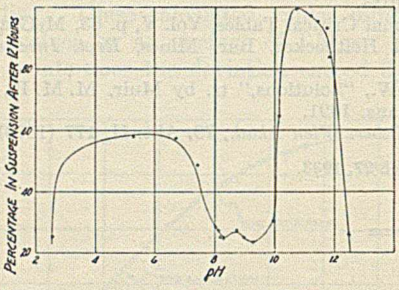

FIGURE 1. PERCENTAGE OF BAROID IN SUSPENSION AFTER 12 HOURS IN A 25 PER CENT WATER DISPERSION AS A FUNCTION OF THE pH

(3) The sealing and plastering action of the colloidal particles contained in the fluid functions as casing, to a certain extent, in preventing caving of unconsolidated formations. This sealing wall acts also as a lubricant for the drill stem and for running a string of casing into the bore hole.

In earlier papers the authors (*2*, *3*) have discussed chemical treatment of clay drilling fluids from the standpoint of colloid physics and have shown that the viscosity of drilling fluid should be maintained at a minimum for adequate control and reclamation of the desirable colloidal content of the fluid. In the present contribution they will report on a study of the control of weighted drilling fluids, with special attention to the stabilization of such dispersions.

WEIGHTED DRILLING FLUIDS

One of the important functions of a drilling fluid is to seal off gas formations by the hydrostatic head of the fluid column. It is possible to hold gas in the formation by the use of heavy drilling fluid which will not only furnish a pressure exceeding that of the gas but also penetrate the formation to a slight extent for the purpose of preventing entrance of gas by diffusion and solution. Suppose the pressure of the gas is 1500 pounds per square inch at 2750 feet; just to balance this pressure, a hydrostatic head of 0.545 pound per square inch per foot is necessary. As water gives a head of 0.434 pound per square inch per foot, the drilling fluid weight per gallon must be at least $8.33 \times 0.545/0.434 = 10.46$ pounds per gallon, where 8.33 is the weight of a gallon of water. In order to furnish a reasonable excess pressure over that of the gas, the fluid should be at least 2 pounds per gallon heavier. It is obvious that clay suspensions of this density are entirely too viscous for pumping, and that a heavier material, such as barytes or hematite, must be used in dispersion to obtain a drilling fluid of the required weight while maintaining the viscosity as low as possible in order that cuttings and entrained gas bubbles may be eliminated at the surface while drilling. The problem of the stability of such a weighted dispersion arises immediately.

One of the most desirable properties of a drilling fluid is the stability of the suspension. In case of enforced suspended circulation of drilling fluid, as when setting casing, it is imperative that the weighting material, together with the cuttings, should remain in suspension to avoid settling around the drill stem and freezing it. Dispersions of most clays are relatively stable, for natural colloids, together with colloid stabilizers such as salts of humic acid, are present therein. Such clay dispersions require no further treatment to increase their suspension qualities until they become loaded with sand and cuttings and the colloids have been partially lost in building up the walls of the bore hole. These fluids may be reclaimed and restored to their original condition by removal of the cuttings, either mechanically or chemically (*2*, *3*), and by small additions of fresh clay if necessary.

The problem of holding weighting materials in suspension is more difficult, however. Such materials as barytes that are ground mechanically do not contain more than a small percentage of natural colloids, such as clay, as a result of weathering action. It should be expected, therefore, that there would be a rapid rate of settling of such a dispersion as barytes in water, for the particles are mostly of larger than colloidal dimension and the specific gravity is high. Both of these factors contribute to increasing the rate of settling by Stokes's law. In actual practice the cost of grinding to colloidal size would be prohibitive, and some other means must consequently be found to suspend these small particles of high density.

Colloids are stabilized by the addition of suitable chemicals—that is, (1) by deflocculation, resulting from the protective action of an adsorbed ion, or (2) by gel formation, with an attendant enormous increase in viscosity in a static condition. Because of the presence of only a small percentage of the emulsoid type of colloid in commercially ground weighting materials, much effect in stabilizing such a suspension with chemicals should not be expected. By far the most logical procedure is to add a cheap colloidal material of the emulsoid type, forming a light gel and thus suspending the heavy particles in a medium that becomes very viscous when in a static condition but which is quite fluid when the suspension is in motion—i. e., the formation of a thixotropic medium. This method has been used to manufacture the commercial weighting material Baroid. A small percentage (2 to 3) of bentonite, or a similar clay, is added as the protective colloid, with the result that a suspension which, without treatment, settles as a sludge within 1 or 2 minutes, is held in suspension indefinitely. This remarkable change is attributable to the formation of a gel by the emulsoid type of colloid present in the bentonite. Fortunately, from a practical viewpoint such treatment does not increase the viscosity of the suspension markedly.

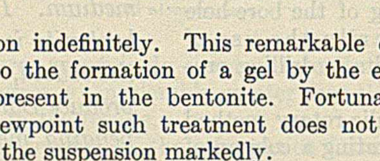

FIGURE 2. PERCENTAGE OF BARIUM SULFATE IN SUSPENSION AFTER 12 HOURS IN A 25 PER CENT WATER DISPERSION AS A FUNCTION OF THE pH

It has now become important to determine the pH for the maximum stability of a suspension of barytes mixed with bentonite. It is known that the pH of bentonite suspensions, as modified by the addition of acid or alkali, has a marked effect on its gelling behavior (*2*). Moreover, barium sulfate has a negative charge, as shown by cataphoretic experiments, in suspensions of a mixture of this material with bentonite, and it follows that the stability of the suspensions should be increased by adsorption of the hydroxyl ion.

This subject has added interest as a result of the recent paper by Parsons (*5*) on the subject. His findings did not check measurements made in the authors' laboratory prior to the publication of his paper. The authors have since repeated this work and will presently show that Parsons' results are seriously in error. The data reported below were secured independently by different workers in the authors' laboratory with different samples of barium sulfate–bentonite mixture, and in all instances identical results were obtained.

LABORATORY METHODS

RATE OF SETTLING. The two general methods for measuring the rate of settling of a suspension are as follows: (1) the rate of formation of free water at the top of the sludge, and (2) the rate of change of concentration at a given reference mark in a column of the suspension.

Robinson (*6*) has given a modified equation for Stokes's law to represent the rate of settling of a suspension as the rate of fall of the top of the sludge:

$$\frac{dH}{dt} = \frac{Kr^2(D - d)}{\eta}$$

where H = height of sludge
t = time of settling
K = a constant
r = average radius of particles
D = specific gravity of particles
d = specific gravity of suspension medium
η = relative viscosity of suspension

This equation, which holds only for suspensions in which the particles are largely of the same radius and specific gravity, has been verified experimentally by application to the data of Adams and Glasson (*1*). The usual weighted drilling fluid made from commercial material contains particles distributed over a considerable range of sizes, and accordingly the measurement of the height of sludge is inaccurate in indicating the percentage settled. In the case of suspensions that are gelled, thus maintaining a substantially uniform sludge in spite of differences in particle size, the method may be sufficiently dependable. But when a gelled condition is not present and the particles are of varying size, the denser and larger particles settle rapidly to the bottom, forming a sediment. In such a case the height of sludge method does not even approximate the percentage settled. Where a drilling fluid is made from the commercial product, Baroid, although a light gel forms and holds the barytes in suspension, several minutes elapse before gel formation, and some of the larger particles settle out.

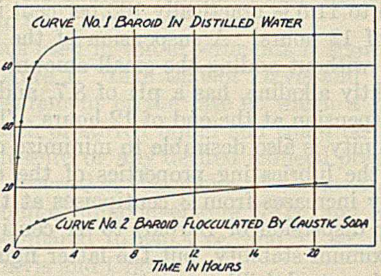

FIGURE 3. RATES OF SETTLING OF 25 PER CENT WATER DISPERSIONS OF BAROID

METHOD FOR MEASURING RATE OF SETTLING. Several procedures of measuring the rate of settling of suspensions, for the purpose of sedimentation analysis, have been described by Odén (*4*). The same general principle underlies all these methods: When a suspension, originally homogeneous, begins to settle after a lapse of time (t) in a layer (x units) under the surface, only those particles that have a rate of settling less than x/t have exactly the same concentration as in the original suspension. The authors' measurements have been made in a series of glass tubes, 3.5 cm. in diameter and 45 cm. in length, with the height of fall constant for each tube at 25 cm. After a given time (t) the liquid is removed to a given mark, and by means of density factors it is possible to determine the percentage of the solid settled from the suspension column or remaining in suspension after a definite time—for example, 12 or 24 hours.

Some measurements have also been made by the height of sludge method. In a series of 8-ounce (236.6-cc.) oil sample bottles filled with the suspension, the height of free water appearing above the settled solids has been taken as the measure of percentage settled.

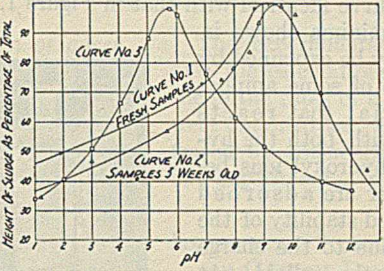

FIGURE 4. PERCENTAGE OF BAROID IN SUSPENSION, MEASURED BY HEIGHT OF SLUDGE IN 25 PER CENT WATER DISPERSIONS AS A FUNCTION OF THE pH

MEASUREMENT OF pH. It has been the experience of the authors that serious errors may result in the measurement of pH values unless the correct method is used and great care is taken to secure equilibrium conditions, especially when the hydrogen electrode is employed. The presence of iron compounds seriously interferes with the attainment of equilibrium in the electrical method of measurement, and great care must be taken to avoid errors. The authors have used three standard methods for these measurements: the hydrogen electrode, the quinhydrone electrode, and indicators. The hydrogen electrode gives satisfactory results over the entire range of pH used from 1 to 14 with Baroid suspensions, but equilibrium is attained very slowly; the quinhydrone electrode is dependable in the range 1 to 8; while the indicators are useful in checking the results obtained with the two electrodes within the range 1 to 13.6. Great care is essential in securing check results by both the electrical method and the indicator method before the observed value is acceptable as final.

DISCUSSION OF RESULTS

Figure 1 shows the percentage of Baroid in a 25 per cent Baroid dispersion in water remaining in suspension after 12 hours as a function of the pH. There are two maxima in the curve, one on the acid side and one of greater magnitude on the alkaline side; the isoelectric point is at pH = 8.7. There is an enormous increase in the stability of the suspension when the pH is increased from the range 8–10 to 10.5–11.5, i. e., an increase from 25 to practically 100 per cent, remaining in suspension in 12 hours. It is evident that it would be advantageous in drilling practice to adjust the pH to the correct range by the addition of caustic soda so as to have a drilling fluid of maximum stability.

The type of curve presented in Figure 1 is similar to the curve obtained by the authors (*2*) for bentonite alone, showing that the bentonite in commercial Baroid reacts with hydrogen and hydroxyl ions to alter the rates of settling of the suspension, with the barytes behaving as inert material. The isoelectric point is practically identical for the two dispersions, and reversal of charge from adsorption of the hydrogen and hydroxyl ions gives maxima and minima at the same pH for the Baroid and also the bentonite dispersion.

In an effort to measure the effect of pH on the rate of settling of barytes, the authors made experiments with dispersions of barytes intended for use as a paint filler and containing no bentonite; but the rate of settling was so rapid that no measurements were possible. To secure the data desired, it was necessary to use a sample of pure precipitated barium sulfate of extreme fineness of size. The results are illustrated in Figure 2, with no maxima in either the acid or the alkaline range and showing very little improvement in stability of suspension. Addition of 2 per cent bentonite (by weight of water of the suspension) to this material resulted in a curve identical with that in Figure 1.

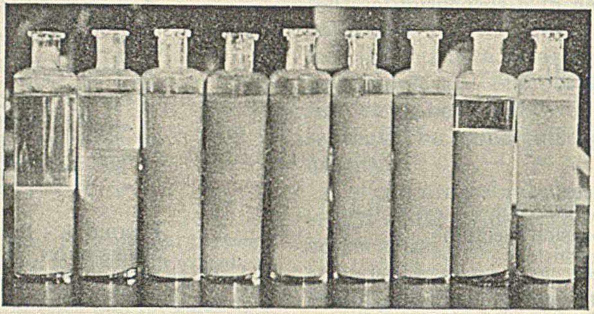

FIGURE 5. SAMPLES OF A 25 PER CENT WATER DISPERSION OF BAROID, WITH VARYING pH, AFTER SETTLING 12 HOURS

The two minima shown in Figure 1 may be explained by the presence of some amphoteric material that reacts chemically with both the hydrogen and hydroxyl ions before the latter are adsorbed with increased stability of the suspension due to the charge imparted to the colloid. At the maximum of the curve on the alkaline side—the point of greatest stability of the suspension—maximum adsorption of the hydroxyl ion has taken place, followed by decrease in stability as a result of the discharging effect of the cation—in this case, sodium ion. Similar relations hold on the acid side.

The viscosity (measured with the Stormer viscometer at 10 revolutions per second) increases on both sides of the isoelectric point from a value of 3 centipoises at a pH of 9 to 41 at a pH of 11.2, approximately the point of maximum stability; this increase would be expected with increased gel formation of the bentonite in the dispersion. The latter figure is not too high for use in actual drilling practice.

Curve 1 of Figure 3 gives the rate of settling for the Baroid suspension in water alone, corresponding to a pH of 8.7 in Figure 1. Curve 2 gives similar data when the suspension has been completely flocculated with caustic, corresponding to a pH of 12.5 in Figure 1. A third curve, corresponding to a pH of 10.5 to 11, would lie along the abscissa axis.

Figure 4 shows the results obtained by the height of sludge method, as used by Parsons. Curve 1 gives the percentage in suspension after 12 hours as a function of the pH, taking the height of the sludge as the percentage of the total height of the column for the ordinate. Photographs of the settling material, such as are shown in Figure 5, provide the data for the construction of the curves. This illustration shows plainly that a relatively large amount of the suspension has settled to the bottom in the bottles showing no free water at the top. This fact demonstrates that the height of sludge method leads to gross errors when the settling particles are not of uniform size. It is obvious that a large amount has settled; but, judging by the amount of free water, the material would be practically 100 per cent in suspension. In other words, the height of sludge method can give the rate of settling of the fine particles only in a suspension with a distribution of sizes. It must be concluded, therefore, that the results of Parsons are seriously in error.

In order to examine the effect of time on Baroid suspensions, a sample 3 weeks old was used to obtain the data given in curve 2 of Figure 4. It is observable that appreciable change has occurred on the acid but not on the alkaline side. This change is not nearly large enough, however, to account for the difference in Parsons' data and those of the authors.

Parsons' data are represented by curve 3 of Figure 4. It is evident that they differ greatly from those presented in this paper, obtained by the same method. This discrepancy may be explained by a difference in the quality of the samples used, particularly a difference in the gelling characteristics of the bentonite.

CONCLUSIONS

It has been shown that the stability of Baroid drilling fluids are greatly influenced by the pH of the suspension. Similar measurements by Parsons, using the height of sludge method, are in error, for this method is not even roughly accurate when applied to a suspension of particles of nonuniform size. According to Parsons' measurements it would be necessary to make the suspension acid (pH = 5.7) in order to have maximum stability (98 per cent in suspension). The authors' measurements reveal that less than 60 per cent of the solids are in suspension at the end of 12 hours under such conditions. The drilling fluid would also have undesirable corrosive properties if stabilized by adding acid to a pH of 5.7.

The authors' measurements by the height of sludge method showed a maximum (100 per cent in stability) at a pH of about 9; but using an accurate method for the case at hand, it was demonstrated that only about 25 per cent remained in suspension at the end of 12 hours at this value of the pH.

A water dispersion of Baroid (10.2 pounds per gallon) at a pH of 10.5 to 11.5 is practically 100 per cent in suspension at the end of 12 hours. A suspension of the same weight using water, without adding the small amount of caustic to make it slightly alkaline, has a pH of 8.7, and only 26 per cent is in suspension at the end of 12 hours. The slight degree of alkalinity is also desirable to minimize corrosion and to improve the lubricating properties of the drilling fluid. The viscosity increases from 3 centipoises at the isoelectric point (water dispersion of Baroid) to 41 centipoises at the point of maximum stability, but the latter figure is not too high for use in actual drilling practice.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of W. T. Schelling, a former member of this laboratory, in making the measurements given in this paper.

LITERATURE CITED

(1) Adams and Glasson, Thesis, Mass. Inst. Tech., 1925.
(2) Ambrose and Loomis, *Physics*, 1, 129 (1931).
(3) Lawton, Ambrose, and Loomis, *Ibid.*, 2, 365; 3, 185 (1932).
(4) Odén, in Alexander's "Colloid Chemistry," p. 861, Chemical Catalog, 1926.
(5) Parsons, *Oil Gas J.*, 29, 95 (Oct. 16, 1930); *Oil Weekly*, 59, 77 (Nov. 7, 1930).
(6) Robinson, IND. ENG. CHEM., 18, 869 (1926).

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CORRECTION. In the article "Empirical Molecular Heat Equations from Spectroscopic Data" by W. M. D. Bryant [IND. ENG. CHEM., 25, 820 (1933)], the second term of Equation 3 should read $\left(\frac{h\nu}{kT}\right)^2$ instead of $\frac{h\nu}{kT}$.

Initial Absorption Rates of Carbon Dioxide by Water and by Dilute Sodium Carbonate Solutions

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A former paper on batch absorption of gases reported that the initial rate of absorption of carbon dioxide by dilute sodium carbonate solution was faster than the initial rate by pure water. Inasmuch as this result has been questioned by other investigators, the experiments have been repeated and the result confirmed.

The theory of liquid stationary films has been developed largely from measurements on batch absorption in liquids. The laws which have been developed should be applied only with caution to gas absorptions in continuous countercurrent tower systems.

IN A FORMER study on batch absorption of gases Davis and Crandall (*1*) found that the initial rate of absorption[1] of carbon dioxide by dilute sodium carbonate was faster than the initial rate by pure water.

In a recent article, Payne and Dodge (*3*) have concluded "that the results of Davis and Crandall are probably in error." The author has therefore repeated the experiments of Davis and Crandall and confirmed their findings. On the other hand, there is no reason to doubt the experimental measurements of Payne and Dodge. These investigators, however, have not taken into account the fact that the conditions in the two cases were quite different—namely, batch absorption by stirred liquids in the case of Davis and Crandall, and continuous countercurrent absorption in a packed tower in their own experiments.

The apparatus used in the experiments is shown diagrammatically in Figure 1. Like that of Davis and Crandall, it permitted measurement of the rate at which a gas was absorbed by a batch of stirred liquid and could be operated at atmospheric pressure or any desired reduced pressure. The volume of the absorption chamber and the area of its cross section at the point of liquid level were 174 cc. and 15.6 sq. cm., respectively, compared to 340.4 cc. and 17 sq. cm. for the apparatus of Davis and Crandall.

To the bottom of the absorption chamber was sealed a glass tube 87 cm. long, and through this ran the glass shaft of a stirrer, as shown. A mercury seal covered the bottom end of the glass tube to a depth of about 10 cm. The glass shaft was attached, by a short piece of rubber tubing, to the top of a flexible steel shaft (from an automobile speedometer) which operated in a U-shaped steel tube. The mercury used in the seal also filled this tube. This method of driving through a mercury seal is superior to that used by Davis and Crandall because there is less friction and the outfit is sturdier. However, the introduction of the stirrer through the bottom, instead of through the top of the chamber, necessitates that the solutions come in contact with mercury, and this might in many cases be objectionable. Further, the liquid between the stirrer shaft and its containing tube (about 8 cc. in this work) mixed with the main body of the liquid only at a slow and uncertain rate.

The experimental methods and the calculations by which the initial rates of absorption were obtained can best be illustrated by considering in detail two experiments.

EXPERIMENT 7 ON ABSORPTION OF CARBON DIOXIDE BY PURE WATER

Distilled water (100 cc.) was placed in the absorption chamber (Figure 1) which was evacuated until the water boiled freely. The connection to the pump was then closed off and the water stirred for about 10 minutes in vacuum, the connection to the pump being opened occasionally to draw off evolved gases. The stirrer was stopped and the stopcock opened to the gas buret containing 100 cc. of carbon dioxide (over 99 per cent pure). Part of this was rapidly drawn into the chamber and, when atmospheric pressure had been reached, readings on the residual gas were obtained as follows:

PERIOD	BURET READING	PROCEDURE
Sec.	*Cc.*	
0	100	Introduction of CO_2 gas started
15	26.4	
25	26.2	
37	25.9	
60	25.7	Stirring started (158 r. p. m.)

PERIOD AFTER STARTING STIRRING		GAS ABSORBED
Min.		*Cc.*
0	25.7	0
0.5	24.2	1.5
1.5	22.0	3.7
(For intermediate readings, see Figure 2)		
146	..	78.1
183	..	79.1

CO_2 absorbed after stirring started, cc. 79.1

CO_2 necessary to saturate 100 cc. water at 25° C. at same pressure 82.8

Difference 3.7

Part of this difference represents carbon dioxide dissolved during the interval between introducing the gas and starting the stirring. Part is probably caused by water around the stirrer shaft which, as explained above, might not have become saturated with the gas.

Curve 7, Figure 2, shows how the rate of absorption of the carbon dioxide into pure water fell off as the quantity dissolved, and therefore its concentration in the solution increased. However, its initial rate of absorption, when the quantity of dissolved carbon dioxide in the main body of the water was negligible, can be readily calculated (*2*).

Let U = the unsaturation of the water in regard to dissolved carbon dioxide at time, t (minutes), expressed as moles of gas (in addition to that dissolved) necessary to saturate the water. Then from the well-known law for the rate of physical solution of a gas (where no chemical reaction is involved),

---

[1] The term "initial rate of absorption" as used here and by Davis and Crandall (reference *1*, pp. 3759–60) refers to the rate when the quantity of gas that has been dissolved is negligible compared to the total at saturation. It is obtained by extrapolating the relationship found experimentally between the absorption rate and the concentration of dissolved gas back to zero concentration. However, as suggested by Nernst, the rate at which the gas is dissolved by the very surface layer itself may be almost infinite. On the other hand, Miyamoto [*Bull. Chem. Soc. Japan*, 6, No. 1, 9–32 (1931)] has made the interesting proposal that among the gaseous molecules which collide with the liquid surface, only those whose components of velocity vertical to the surface are greater than a threshold value are able to enter the liquid phase.

$$-\frac{dU}{dt} = KU \text{ or } -d \ln U = Kdt$$

How accurately this relationship held in experiment 7 is seen by the linear relationship of log U and t in Figure 3.

Now $$K = \frac{1}{t} \ln \frac{U_0}{U}$$

and its value can be conveniently calculated from the time required for U to fall to half value (in this experiment 26 minutes) so that $K = 0.027$.

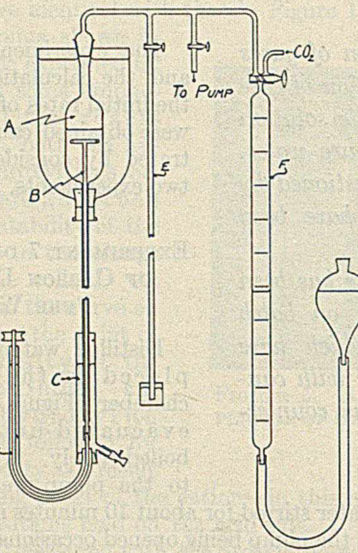

Figure 1. Apparatus for Measuring Rates of Gas Absorption by Liquid

- *A.* Absorption chamber
- *B.* Stirrer operating in tube longer than barometric height
- *C.* Mercury seal
- *D.* Flexible steel drive operating in mercury.
- *E.* Mercury manometer
- *F.* Gas buret

The total unsaturation of the 100 cc. of water before any carbon dioxide dissolved was 32×10^{-4} moles, so that under these experimental conditions the total initial absorption rate of carbon dioxide by 100 cc. of water at 25° C. and 760 mm. total pressure would be 0.85×10^{-4} moles per minute, and the rate per square centimeter of liquid surface, 91×10^{-9} moles per sq. cm. per second.

Experiment 8 on Absorption of Carbon Dioxide by Dilute Sodium Carbonate

Curve 8, Figure 2, shows the rate of absorption of carbon dioxide by a 0.17 M solution of sodium carbonate under conditions similar to its absorption by pure water in Experiment 7. The rate fell off only slowly with the quantity absorbed, so that it was easy to calculate the initial total rate directly from the absorption curve, 1.6×10^{-4} moles per minute. This was nearly twice the initial rate into pure water under similar conditions.

Experiment 6, Table I, confirms an experiment of Davis and Crandall in which the absorption rate into 0.1 M sodium hydroxide was followed until no more gas was absorbed. The rate at half neutralization (experiment 6A) was approximately half the initial rate, and the total quantity of carbon dioxide absorbed corresponded to that necessary to form bicarbonate and to saturate the solution physically. The initial rate of the final physical saturation was somewhat more than half that at the point of half-neutralization.

Table I gives the results of the eight experiments carried out in the apparatus and also of three experiments from the work of Davis and Crandall. It is evident that stirring at the same speed in different apparatus does not indicate the same degree of agitation. Thus the efficient stirrer used in the present experiments gave about the same absorption rate by water at 158 r. p. m. (experiment 7) as did that of Davis and Crandall at 400 r. p. m.

Table I. Rates of Absorption of Carbon Dioxide per Unit Area, in Batch Absorptions

Expt.	Liquid	Rate of Stirring *R. p. m.*	Initial Absorption Rate per Unit Area *Moles/sec./sq. cm.*	Av. ($\times 10^{-9}$)
	Preliminary			
1	100 cc. water	192	126	133
2	100 cc. water	192	131	
3	100 cc. water	192	140	
4	100 cc. 0.17 M Na_2CO_3	192	171	
5	100 cc. 0.10 M NaOH	192	358	370
	Final			
6	100 cc. 0.10 M NaOH	192	382	
6A	100 cc. 0.05 M Na_2CO_3	192	175	
7	100 cc. water	158	91	
8	100 cc. 0.17 M Na_2CO_3	151	167	
	EXPERIMENTS OF DAVIS AND CRANDALL			
2	100 cc. water	400	94	
4	100 cc. 0.1 M NaOH	400	218	
5	100 cc. 0.1 M Na_2CO_3	400	235	

Experiments 1 to 5 may be considered preliminary because the absorptions were not carried to completion. However, without exception, they as well as the final ones confirm the findings of Davis and Crandall—that in batch absorptions of this type the initial rate of absorption of carbon dioxide by dilute sodium carbonate solutions is faster than the initial rate by water under similar conditions.

However, the absorption rate into sodium carbonate was not greatly affected by changes in the rate of stirring or the concentration of the solution (experiments 4, 6A, 8) whereas the rate into pure water increased with stirring (experiments 1–3, 7). From the standpoint of the unstirred liquid-film theory, this would indicate that it is only in the case of slowly stirred liquids, or in thick film absorption, that the reaction to bicarbonate in the film predominates. When the film becomes very thin, the greater bulk of this reaction takes place in the main body of the solution. In any case of batch absorption, where the quantity of liquid in the film is negligible compared to that in the main body of the liquid, the reaction to bicarbonate should keep the concentration of dissolved carbon dioxide in the main body very low. The initial absorption rate should then never be less than that into pure water.

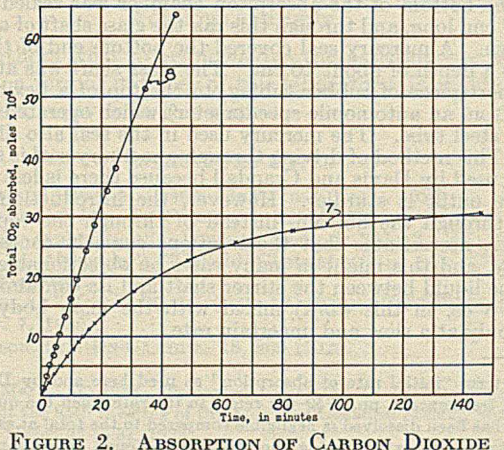

Figure 2. Absorption of Carbon Dioxide

7. Into free water. 8. Into 0.17 M sodium carbonate.

It is quite otherwise, however, in tower absorption experiments such as those of Payne and Dodge. Here the whole liquid is in the form of thin layers, some of which are probably comparable in thickness with the stationary films on the surface of slowly stirred liquids. There is no large stirred body

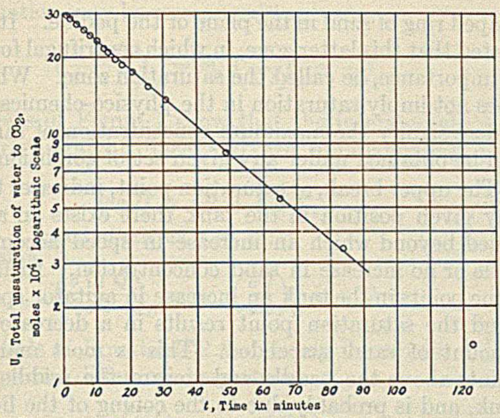

FIGURE 3. ABSORPTION OF CARBON DIOXIDE BY WATER (EXPERIMENT 7)

of liquid in which concentrations are moderately uniform throughout the body and in which slow reactions can be completed.

The liquid stationary (or unstirred) film theory is based mainly on the laws which have been found regarding the rates of solution of solids and gases by batches of stirred liquids. These laws should be applied only with caution to absorptions where the area of the liquid interface is very great compared to the liquid volume.

LITERATURE CITED

(1) Davis and Crandall, *J. Am. Chem. Soc.*, 52, 3757, 3769 (1930).
(2) Davis, Thomson, and Crandall, *Ibid.*, 54, 2345 (1932).
(3) Payne and Dodge, IND. ENG. CHEM., 24, 630 (1932).

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Studies in Agitation

II. Sand Concentration as Function of Sand Size and Agitator Speed

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The distribution of sand under the influence of a simple paddle agitator has been studied for various sizes and amounts of sand, for various agitator speeds, and at various positions in the tank. It is found that the curves of sand concentration vs. agitator speed show three distinct zones, corresponding respectively to absence of strong vertical currents, marked vertical currents, and marked centrifugal forces (saturation). The curves for various sand sizes have been correlated empirically, a plot of log Q/D^m against R yielding a straight line for each of the two lower zones. It is suggested that the position of the saturation point (that is, the agitator speed at which maximum concentration is obtained) may be used as a criterion of intensity of agitation.

IN A PREVIOUS communication (*2*) the distribution of a roughly screened sand was described for various positions in a tank equipped with a simple paddle agitator. It was shown that uniformity of concentration was never attained, and that there was a hydraulic classifying action on the part of the agitator, the fines tending to move toward the wall of the tank while the coarser particles tended to concentrate in the center of the tank under the paddle. This effect was deemed worthy of further study, and in the present paper are presented data showing the influence of agitator speed on the distribution of sand of various sizes when varying total amounts of sand are present.

EXPERIMENTAL PROCEDURE

The equipment used in these tests was the same as that previously described (*2*). Briefly, it consists of a cylindrical steel tank 4 feet 4 inches (1.32 meters) in diameter equipped with a simple paddle stirrer with a blade 2 feet 1 inch (0.64 meter) long. The water level in the tank was, as before, held arbitrarily at 2 feet (0.61 meter) above the bottom of the tank, corresponding to 220.5 gallons (835.7 liters) of water. The paddle was kept in the low position, with its lower edge 5.25 inches (13.34 cm.) from the bottom of the tank.

Sampling and analysis of samples were carried out in the manner previously described except that samples of about 500 cc. were taken, to reduce sampling errors, instead of samples of about 125 cc. The agitator was operated for about 15 minutes before samples were taken to insure the attainment of a steady state. The sand used was carefully screened to size, the four fractions selected for study being those trapped between 32 and 42 mesh, between 48 and 65 mesh, between 65 and 100 mesh, and between 80 and 150 mesh Tyler standard screens. The sand was washed following screening.

For each sand size, tests were run varying the agitator speed while holding constant the total amount of sand and water. The agitator speeds varied from velocities so low that sand could barely be detected in suspension to speeds so high that there was marked coning of the surface of the water and slight splashing, a range of 18 to 88 r. p. m. For the 32–42 and 65–100 mesh fractions the effect of varying total amount of sand with constant amount of water was studied at various agitator speeds.

Results could be duplicated satisfactorily. However, checks were more difficult to obtain in the area immediately around the paddle than at points nearer the wall of the tank. Checks were also less satisfactory at very low sand concentrations, particularly with the larger sand sizes.

EXPERIMENTAL RESULTS

In Figure 1 are plotted curves showing the concentration of sand in milligrams per 100 cc. of water, as a function of agitator speed for the sampling point 2 inches (5 cm.) from the wall and 2 inches from the bottom of the tank. For each of the four sand sizes a total of 15.5 pounds (7 kg.) of sand was used. The curves for the finer sand sizes show three distinct zones—one a comparatively flat curve at low agitator speeds indicating a rapid increase in sand concentration with velocity, the second a steeper curve which terminates in the

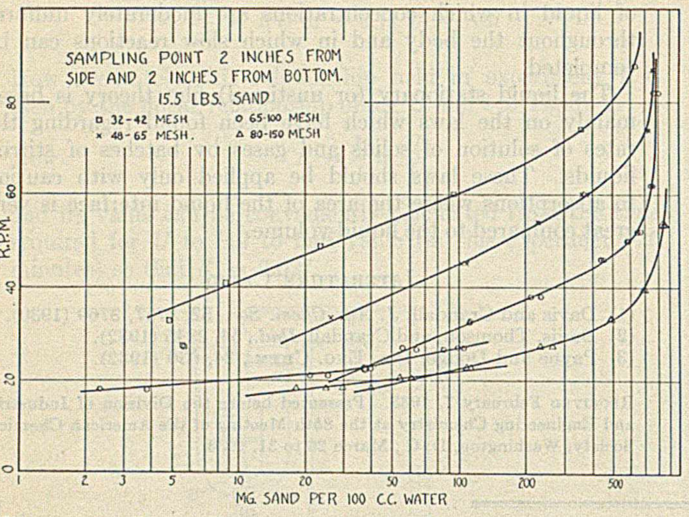

FIGURE 1. SAND CONCENTRATION AS FUNCTION OF AGITATOR SPEED FOR VARIOUS SAND SIZES

third (or vertical) zone in which increase in agitator speed has little effect on sand concentration.

Hixson and Crowell (*1*) have noted three regimes of agitation when solid salt is stirred with water. They report that at low agitator speeds a "passive or nonflow" regime is maintained in which the solid particles remain on the bottom of the container with little or no motion. At somewhat higher speeds the particles move inward toward the center of the tank, a regime characterized by these authors as curvilinear flow. At high agitator speeds the particles of salt were thrown outward from the center, and the regime described as turbulent flow was established. It has been suggested that the regime at low agitator speeds is one in which the vertical currents set up by the agitator are not sufficient to raise the sand particles from the bottom of the tank, while the intermediate zone is one in which vertical currents are of sufficient magnitude to produce considerable suspension of sand, the amount thus suspended being a function of agitator speed. In the third, or high-speed, zone centrifugal forces are becoming sufficiently strong to combat effectively the forces tending to produce a more uniform sand concentration. These conclusions have been confirmed by a study of the motion of sand particles in a glass scale model of the apparatus used in the large-scale experiments. As the agitator speed was slowly increased, the sand began to move slowly in a spiral path across the bottom of the container, forming a cone under the center of the paddle. With increasing speed more and more sand was picked from the surface of the cone and drawn into the paddle, while the sand flowing across the bottom of the tank increased in amount. At high speeds the cone of sand entirely disappeared, giving place to a doughnut-shaped ring of sand in the plane of the paddle. It is suggested that this latter zone, in which centrifugal forces are of importance, be called the saturation zone. While this does not imply saturation in the physico-chemical sense, it does signify the maximum concentration of sand that can be obtained under any given set of conditions.

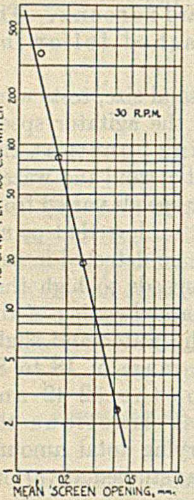

FIGURE 2. SAND CONCENTRATION AS FUNCTION OF SAND SIZE AT CONSTANT AGITATOR SPEED

The upper break, or saturation point, indicates that for any given position in the tank there exists an agitator speed beyond which an increase in speed accomplishes little or no increase in sand concentration. In fact, for some points in the tank an increase in agitator speed beyond the saturation point results in a decrease in the amount of sand suspended. This is most marked at points above the paddle and toward the middle of the tank, and is probably due to the coning of the liquid at high agitator speeds. Calculation indicates that the sand concentration at saturation is almost always less than the concentration which would be attained if all the sand in the tank were uniformly suspended, except at points beneath and immediately beyond the paddle. The sand has a marked tendency to remain under the paddle, and here very high concentrations are attained.

Although Figure 1 presents data for but one position in the tank, the curves for the other positions are similar to those given. As noted above, however, the saturation curves for points near the middle of the tank have negative slopes.

While no theoretical treatment seems possible at present owing to lack of data on the velocity of the water relative to the sand in various parts of the tank, it has been possible to correlate empirically the effect of sand size, sand concentration, and agitator speed, for a given position in the tank and a given total amount of sand. If from Figure 1 are read values for sand concentration at constant agitator speed for the four sizes tested, and these values are plotted on log-log paper against the logarithmic mean clear opening of the screens forming the limits of the fractions chosen, a straight line results, as shown in Figure 2. A very limited range of agitator speeds is available for drawing this line, for a slightly higher r. p. m. than the one indicated falls on the saturation curve for the 80–150 mesh fraction. The equation of the line drawn may be represented as:

$$\log Q = m \log D + \log K_1 \tag{1}$$

where Q = sand concentration, mg. per 100 cc. water
m = slope
D = logarithmic mean clear opening of screens forming limits of fraction

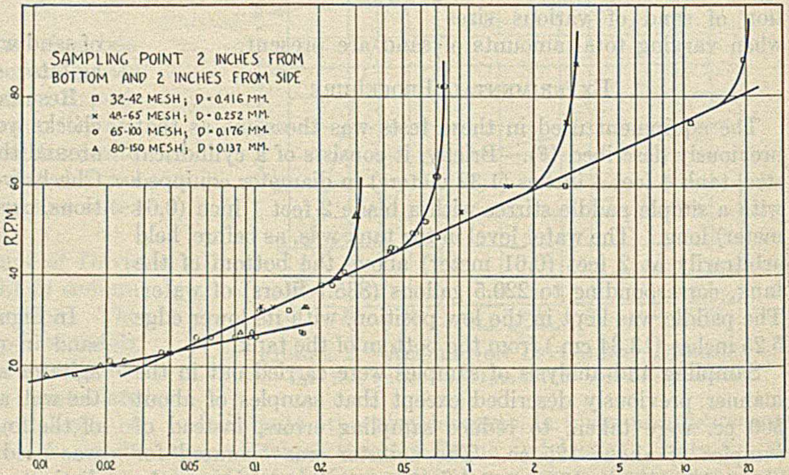

FIGURE 3. RELATION BETWEEN SAND SIZE, SAND CONCENTRATION, AND AGITATOR SPEED

This equation may be rearranged to give:

$$\left(\frac{\delta \ln Q}{\delta \ln D}\right)_R = m; \left(\frac{\delta Q}{\delta D}\right)_R = \frac{mQ}{D} \qquad (2)$$

The curves of Figure 1 show that the intermediate portions are nearly straight lines and are approximately parallel; hence,

$$\log Q = \mathrm{n}R + \log K_2 \qquad (3)$$

where R = speed of stirrer, r. p. m.
Rearranging,

$$\left(\frac{\delta \ln Q}{\delta R}\right)_D = \mathrm{n}'; \left(\frac{\delta Q}{\delta R}\right)_D = \mathrm{n}'Q \qquad (4)$$

The partials of Equations 2 and 4 may be substituted in the general partial differential equation:

$$dQ = \left(\frac{\delta Q}{\delta R}\right)_D dR + \left(\frac{\delta Q}{\delta D}\right)_R dD \qquad (5)$$

giving

$$dQ = \mathrm{n}'Q\, dR + \frac{mQ}{D} dD \qquad (6)$$

On separating variables and integrating, it is found that

$$\log Q/D^m = \mathrm{n}'R + \log K_3 \qquad (7)$$

This is the equation of a straight line. From Figure 2, for the point 2 inches from the side and 2 inches from the bottom of the tank, the slope of the log Q vs. log D curve is -4.0. This is therefore the value of m to be substituted in Equation 7. Plotting the logarithm of Q/D^{-4} (or its equivalent logarithm QD^4) against R, a straight line results, from which branch perpendicularly the saturation curves for the various sand sizes. The passive-flow curves likewise form a single line, as shown in Figure 3. From this relation it should be possible to interpolate and, to a limited extent, extrapolate to determine the behavior of an untested sand size.

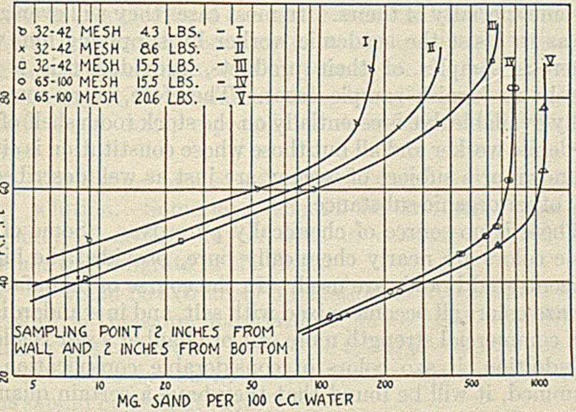

Figure 4. Effect of Varying Total Amount of Sand

If plots similar to those of Figures 1 and 2 are made for other positions in the tank, and the value of the constant m is inserted in Equation 7, new curves are obtained differing from those in Figure 3 in that they are displaced horizontally. The curves in the passive-flow region, however, show very little change in position. Fair correlation is obtained by the general use of the value -4 for the exponent m, but better results are obtained by determining for each point its own value of this slope. The slope of the log Q/D^m vs. R curve seems to be fairly constant throughout the tank. As would be expected, the transition point occurs at different agitator speeds in various portions of the tank, since liquid velocity is not a simple function of agitator speed.

The amount of sand at saturation (taken as the maximum concentration obtained at any given point) seems to be a power function of the sand size. By plotting the logarithm of the sand concentration against the logarithm of the mean clear opening of the screens, an approximate straight line is obtained. The slope of this line varies widely from point to point in the tank, however, being negative in some cases and positive in others. The above relation therefore seems to be at best an approximation.

In Figure 4 are plotted curves showing sand concentration as a function of agitator speed for varying amounts of sand. The left-hand curves refer to the 32–42 mesh sand, with 4.3, 8.6, and 15.5 pounds (1.96, 3.9, and 7 kg.) present. The right-hand curves refer to the 65–100 mesh sand, with 15.5 and 20.6 pounds (9.3 kg.) present. The sand concentration increases as the total amount of sand is increased. There is a strict proportionality between amount of sand and sand concentration at saturation. This is shown in Figure 5, in which sand concentration is plotted against total amount of sand present for each sand size. At velocities below the saturation point, sand concentration does not increase as rapidly as the amount of sand, and the curves obtained are roughly parabolic. No explanation of the increase in sand concentration with amount of sand is offered at this time, as variables other than those studied seem to be involved. However, the density of the system does not seem to be an important factor since variations in the apparent mean density of the suspension are small in comparison to the magnitude of change in concentration with amount of sand.

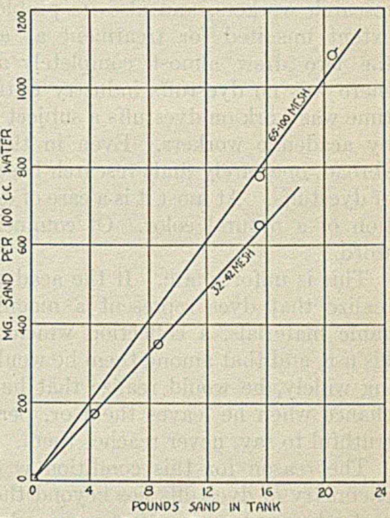

Figure 5. Sand Concentration at Saturation as Function of Total Amount of Sand

Saturation Point as Measure of Agitation

Since the saturation point occurs at approximately the same agitator speed for different points in the tank if the sand size and total amount of sand are held constant, it is suggested that the agitator speed at which saturation occurs might be used as a measure of intensity of agitation. For a given position in the tank, preferably near the wall and somewhat above the paddle, and with a standard amount of standard size sand, samples could be obtained at various agitator speeds. The paddle giving the highest sand concentration at the saturation point could be considered as most effective in distributing the solid. Such tests should be paralleled by power demand studies, which, in the light of the saturation point, might be interpreted in such a way as to determine the optimum agitator, or the agitator which accomplishes the distribution of solid most effectively for a given power demand. Further work along this line is in progress.

Acknowledgment

The authors are indebted to B. E. Lukens for assistance with the experimental work.

Literature Cited

(1) Hixson and Crowell, Ind. Eng. Chem., 23, 1161 (1931).
(2) White, Sumerford, Bryant, and Lukens, *Ibid.*, 24, 1160 (1932).

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Dyestuffs as Field for Academic Research

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THE dyestuffs industry arose from work done by academic investigators, and for a long time the relation between the university laboratory and the industry was fundamental to the progress of the latter. But, as the industry grew, it came to rely more and more upon its own research workers, and also its problems became to a larger extent unsuited for treatment as academic research until the two drew almost completely apart. In this country there was no dyestuffs industry until of late, so that at no time was work on dyestuffs a subject chosen for investigation by academic workers. Even in the reports of work done abroad, one rarely finds research based on the characteristics of dyestuffs. At most it is a case of determining the constitution of a natural color. Of commercial dyes one finds no word.

This is unfortunate. If the academic chemist would only realize that dyes represent a magnificent collection of organic materials, a collection which is readily available for his use, and that among them he would find substances differing widely, he would realize that he is missing an excellent chance when he leaves them or, perhaps it would be more truthful to say, never reaches them.

The reason for this condition is not far to seek. The chemistry of dyestuffs lies beyond the region of the ordinary and advanced courses in organic chemistry. These do not contain much more than a reference to the triphenylmethane colors, perhaps going so far in the advanced course as to discuss the constitutional formula of rosaniline, *p*-rosaniline, and the basic violets. There will be some description of the diazo reaction and of its use in making a dye, the example chosen being usually methyl orange. Add to this a full discussion of von Baeyer's work on the constitution and the synthesis of indigo and you have most of the material furnished in the organic courses available with one exception—the work on the determination of the constitution of Turkey red. I am afraid both instructor and student believe that this is one of the most important of dyes. Formerly it was, but now real Turkey red would be hard to find in any store.

This is not said in any spirit of criticism. After all, the whole field is much too broad to be covered in detail and there are many more adaptable chapters than those describing dyestuffs. Dyes merely as examples to illustrate monoazo, disazo, and trisazo couplings are not very interesting. Indeed, there is no group less interesting if viewed merely superficially. I can remember my own consternation when I was forced to meet the difficulty of giving a course on dyes to an advanced class. The triphenylmethane group was not so bad; I could go over the logic used by the organic chemists who determined the real constitution of these bodies. But the azo group was hopeless because it was merely a case of describing variants on a single reaction and stating that the product obtained was yellow, red, orange, or blue, as the case might be. The real subtlety of these materials escaped me entirely because I was not familiar with the dyer's art and I could not see how every molecule that I described was actually an admirable material to meet the special needs of the user.

Hedged around by the limit of commercial availability, the dye chemist had built marvelous molecules, each subtly different from the other, but I did not see clearly enough to read the meaning of those delicate variations in the choice of intermediates for special results. In fact I had a feeling that dyes, being such practical materials, were a little beneath the mental ability of the synthetic organic chemist. I suffered from the delusion that a product synthesized in a chemical factory was in some way contaminated by the atmosphere of useful research instead of being born of pure academic genius.

And the dyes themselves are another deterrent. They are not available on the shelves of the supply houses except for some few ordinary indicators and stains. They are not available as beautiful, chemically pure, crystalline substances. After all, what is there to make a student or his professor think of using a direct black azo dye for determining the effect of electrolyte concentration on the rate of diffusion of a colloidal organic substance? Again, dyes are known by cryptic trade names. These alone are sufficient facts to deter the academic worker.

CHEMICALLY PURE DYES

But these difficulties may be surmounted in order to reach the abundant treasure that is actually available. While it is true that the chemical identity of dyes is not disclosed on the label nor is it found in the ordinary textbook, the identity can be established easily by taking a little trouble. The laboratories of the dyestuffs manufacturers and the pages of the Colour Index published by the Society of Dyers and Colourists are available for consultation. The dyestuffs manufacturers are willing to answer honest inquiries. They are glad to stimulate research in their field. Of course one cannot expect them to be willing to disclose the constituents of some specialty of theirs. In most cases they will even go so far as to assist the academic worker by supplying him with generous samples of their products, provided this is not merely to furnish sample cases. Therefore, every commercially available dye is essentially on the stock room shelf of the academic worker and all but those whose constitution is either unknown or a subject of secrecy are just as well described as any other organic substance.

There is no source of chemically pure dyes. Some of the basic colors are nearly chemically pure, provided the highly concentrated brands are used. In the course of manufacture the azo colors all become mixed with salt, and in standardizing to a commercial strength more salt or Glauber's salt is added. In addition, if azo colors of considerable complication are examined, it will be found that they have a certain quantity of material other than the chief component, simply because it is not possible to carry out a coupling quantitatively on a manufacturing scale.

The purification of dyes is not particularly difficult in comparison with other complex organic substances. The literature contains descriptions of the best methods for purifying such dyes as Congo red.

I can recommend a method which I have worked out. This is to precipitate the dye as an organic salt. The best base for this purpose I have found to be one of those aryl guanidines which are used as vulcanization accelerators. These are available at a low cost and in a condition of great purity. I have found the most serviceable to be diphenyl- and di-*o*-tolylguanidine. Once in a while triphenylguanidine may come in handy because its salts are much less soluble. If a solution of the hydrochloride of such a base is mixed with the hot solution of the dye, a tarry precipitate is formed at once. This can usually be collected on a glass rod, solidified on cooling, and, after cooling, be broken up, washed with water containing a little more of the hydrochloride, and finally dissolved in methanol. It can then be filtered and the alcohol evaporated off, or, in some cases, sodium methylate may be added in sufficient quantity to precipitate the sodium salt from the alcoholic solution. In general I have found it better to evaporate the alcohol completely and add the theoretical quantity of sodium or potassium hydroxide. Alcohol can then be added until the sodium salt separates out. It is filtered off and extracted with alcohol until the liquor is colorless if the dye is really insoluble in alcohol or until the extraction has reached the stage represented by the maximum solubility of the sodium salt in alcohol. Going through this process once gives one an extremely pure dyestuff but, if necessary, it can be repeated. The process eliminates the more soluble organic impurities that were formed as by-products in the process of manufacture, if it is carried out in such a way that the original dye is not completely precipitated by the guanidine salt. Some of these guanidine salts can be recrystallized from organic solvents, usually alcohol, or alcohol and water.

Assuming that we have purified our dyestuffs, what can we do with them? What sort of problems are available?

Physical Problems

1. The physical properties of dyes have not been settled by any means. I should like to see the solubility of pure dyes, at temperatures up to those employed in dyeing, determined quantitatively. This should include solutions containing the usual dyeing assistants—sodium chloride and sodium sulfate.

2. Practically nothing is known about the true solubilities of the calcium, magnesium, iron, and aluminum salts of dyes.

3. When dyeings of vat colors and azo colors are soaped, the hue is changed, and the fastness to light is distinctly improved, presumably because of a change in particle size. The actual mechanism of this process would furnish an excellent subject for research, even though a great deal has already been done, especially in connection with the azo colors.

4. The dyeing of acetate rayon is stated to be a case of solid solution. Something should be known of the real solubility of acetate rayon dyes in cellulose acetate, and whether they migrate in the fiber.

5. It would be extremely interesting to dye a whole series of colors on the same material in equimolecular percentages. In doing this care would have to be taken to consider the dyestuff left in the dye bath; for this reason very low concentrations should be used at first.

6. The quantitative measurement of the equilibrium relation between the dye on the fiber and in the bath throughout the dyeing process in the case of rayon and cotton at high and at lower temperatures needs investigation.

7. It would be interesting to determine the properties of dyestuffs as applied to cotton, wool, and silk in other than aqueous solution—in liquid ammonia, sulfur dioxide, and organic solvents. For the latter the salts of organic bases can be used.

8. The diffusion rates of dyes under dyeing conditions and the use of the results to calculate the particle size of these substances has been investigated to some extent but there is a great deal still to be done.

9. The change in the equilibrium point between the dye in the dye bath and on the fiber which is produced by the addition of dispersing agents, such as glue, is of material interest to the dyer and has never been determined accurately.

10. The rate at which the final equilibrium between the dye in solution and on the fiber is reached is a characteristic of the dye which determines how it will behave in continuous dyeing, particularly when used in combination with other dyes. The dyer's method of determining the rate of exhaust is practical. We should have a quantitative method which would describe the rate at which the dye which goes on to the fiber is adsorbed and the total percentage of the available dye which is adsorbed. These two characteristics are quite independent.

11. In the case of lake colors which are used in printing inks, one of the important characteristics is oil absorption. The underlying causes of the differences are practically unknown and yet one lake will make so stiff an ink that it will be useless while another will be quite fluid. Presumably this is a matter of particle size, but it goes back to the characteristics of the dye used in making the lake.

Chemical Problems

1. The nature of the reaction by which "indigosols" undergo oxidation should be investigated. The "indigosols" are esters of reduced vat colors. They oxidize readily when treated with such substances as ferric salts or nitrous acid. The reaction then is a saponification and oxidation or the two steps in the reverse order.

2. During the printing of vat colors the pastes give off gaseous substances which are important in their effect on the development of the prints of certain colors. Very little is known about these products.

3. Colors that are quite fast to light on paper or as paper dippings are sometimes extremely fugitive in nitrocellulose lacquers. This is particularly true of azo colors. Presumably the nitrocellulose acts as an oxidizing agent. The nature of the reaction is unknown.

4. A method for removing the sulfonic acid groups from the azo colors without destroying the dyestuff would be useful. If anyone is looking for something desperately difficult, here is the problem.

5. An interesting subject for research would be that of comparing the effects produced by a change in the position of one substituent at a time on the finer physical characteristics of the dyestuff molecule. For example, in the case of benzidine coupled with two molecules of H acid, we are dealing with a direct blue which is distinctly colloidal in its characteristics. Now, if we leave the H acid on one side but substitute Chicago acid on the other, we have done nothing but shift the position of two sulfonic acid groups. What differences will this cause in the behavior of the colloidal particle? Perhaps none, but so far as the writer knows, except for the variation produced in the hue of the dye, the differences have never been investigated. We have any number of colloidal substances but few of them allow of such delicate variations being played upon their chemical constitution. In the case being used as an illustration, we could next substitute one molecule of K acid in which the two sulfonic acid groups are altered in their relative position, one occupying the same position as in the original H acid. We could go farther and choose compounds in which the position of the amino and hydroxyl groups differed. The variations are practically limitless and each change in constitution could be followed exactly. Again it would be just as easy to modify the benzidine by substituting tolidine or dianisidine while leaving the sulfonic acid groups in the H acid unaltered. There is a wonderful field for the physical chemist in such treatment of the constitutional variations which are possible in those colloids which are dyes.

In closing, I wish to advise the academic worker never to undertake research on any phase of dyestuff chemistry without consulting a competent dyestuff chemist. The pitfalls are so numerous that he is almost certain to overlook some one of them. He is apt to think, for instance, if he is unfamiliar with the field, that, if he gives the name of the dye, he has described it sufficiently minutely. As a matter of fact, this is not so, because dyes are not found in commerce as chemically pure substances. Also, while I am a great believer in the value of academic research and of its being untrammeled by any effort to make it practical, yet it seems foolish not to make academic work fit into the practical use of products if we can do so without causing the academic work to suffer. For instance, I do not see any advantage in a study of lake formation using dyestuffs that are not sufficiently adapted to the production of commercial lakes to rank as lake colors. The idea of synthesizing valuable dyestuffs in the course of anything but long continued and specialized work in the field is bound to be disappointing. Synthetic work having for its object the production of useful dyes I would regard as the least promising of all fields for the academic worker.

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Preparation of 1,2- and 2,3-Diaminoanthraquinones

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In the preparation of 3′,4′-dichloro-2-benzoylbenzoic acid, a study of the effect of time, temperature, solvent ratio, and agitation on yield and purity of the product is reported. The maximum yield is 80 per cent.

Cyclization of the keto acid by means of concentrated sulfuric acid gives in all instances a mixture of the isomeric dichloroanthraquinones. Difference in solubility of each isomer in sulfuric acid and also in ethanol indicates the quantitative relationship of 13 per cent 1,2-dichloroanthraquinone to 87 per cent 2,3-dichloroanthraquinone.

Ammonolysis of the corresponding dihalogenoanthraquinones, in the presence of copper, an oxidant, and ammonium nitrate, results in the complete removal of chlorine.

THIS report deals with the utilization of 1,2-dichlorobenzene as a raw material for the preparation of 1,2- and 2,3-diaminoanthraquinones. These isomeric compounds have been previously prepared by more complex methods. Briefly, the procedure employed in this case was the condensation of phthalic anhydride with 1,2-dichlorobenzene, in the presence of anhydrous aluminum chloride, to yield 3′,4′-dichloro-2-benzoylbenzoic acid, which was cyclized to a mixture of the isomeric 1,2- and 2,3-dichloroanthraquinones. Conditions were found under which the separated isomers were aminated to the corresponding diaminoanthraquinones.

A critical examination of the available technical 1,2-dichlorobenzene indicated the presence in practically all cases of varying quantities of 1,4-dichlorobenzene, chlorobenzene, and traces of polychlorinated benzenes. By means of refrigeration and distillation, a relatively pure 1,2-dichlorobenzene was obtained, which contained as the only impurity a trace of 1,4-dichlorobenzene. Carswell (*3*) reports the boiling point of pure 1,2-dichlorobenzene to be 180.3° C. It was possible to secure for this work a special product which gave a distillation range of 179.5° to 180.5° C.

Preparation of 3′,4′-Dichloro-2-Benzoylbenzoic Acid

Senn (*8*), Phillips (*6*), and later M. and N. Tanaka (*9*) reported the preparation of 3′,4′-dichloro-2-benzoylbenzoic acid by the condensation of phthalic anhydride with 1,2-dichlorobenzene in the presence of anhydrous aluminum chloride.

In the present investigation a study was made of the effect of time, temperature, solvent ratio, and agitation, in an attempt to improve the purity and yield of the keto acid. The equipment employed is shown in Figure 1. Tables I–III illustrate the effect of the variables listed. The phthalic anhydride, anhydrous aluminum chloride, and 1,2-dichlorobenzene were mixed together and treated under the conditions indicated in the tables. After the reaction was completed, the mass was hydrolyzed with cold dilute mineral acid, the excess of 1,2-dichlorobenzene was removed by steam distillation, and the aluminum was removed as a salt in solution. The soluble ammonium salt of the keto acid was obtained by treating the residue with aqueous ammonia. This was passed through a filter to remove insoluble impurities, and the keto acid was reprecipitated by the addition of mineral acid. The 3′,4′-dichloro-2-benzoylbenzoic acid was then collected on a filter, washed, dried, and weighed.

Table I. Effect of Solvent Ratio on Preparation of 3′,4′-Dichloro-2-Benzoylbenzoic Acid

Phthalic anhydride, 0.5 mole = 74.0 grams
Anhydrous $AlCl_3$, 1 mole + 10% = 147.8 grams
1,2-Dichlorobenzene = 0.5 mole × ratio
Solvent = excess 1,2-dichlorobenzene
Theoretical yield = 147.5 grams
Reaction time = 8 hours
Reaction temp. = 90° C.
M. p. of pure keto acid = 192.5° C.
M. p. of crude keto acid, all runs = 190–191° C.

Expt.	Solvent / Phthalic Anhydride	Type of Agitation	Yield	
	Moles		*Grams*	*% of theory*
1	2/1	None	35.4	24.0
2	3/1	None	95.0	64.4
3	4/1	None	96.5	65.4
4	5/1	None	98.0	66.4
5	6/1	None	99.0	67.1
1-A	2/1	Continuous	92.3	62.6
2-A	3/1	Continuous	96.2	65.2
3-A	4/1	Continuous	101.2	68.6
4-A	5/1	Continuous	104.0	70.5
5-A	6/1	Continuous	106.0	71.8

Preparation and Separation of Isomeric Dichloroanthraquinones

Senn (*8*) reported 87 per cent of 2,3-dichloroanthraquinone and 13 per cent of 1,2-dichloroanthraquinone from the cyclization of 3′,4′-dichloro-2-benzoylbenzoic acid. He made the cyclization with concentrated sulfuric acid and effected a separation of the isomers by the difference in their solubility in the residual acid. M. and N. Tanaka (*9*) state that they obtained 2,3-dichloroanthraquinone in the condensation of 1,2-dichlorobenzene with phthalic anhydride in the presence of aluminum chloride at 130° to 150° C. As might have been expected, neither the yield nor the purity of the product was satisfactory.

None of the various dehydrating agents tried were as satisfactory for this cyclization as sulfuric acid. Preliminary experiments in ring closure indicated the presence of both the 1,2- and 2,3-dichloroanthraquinones. In an effort to increase the quantity of the more valuable 1,2-isomer, cyclizations were made with the following variables: time, acid ratio, acid concentration, and temperature. A higher temperature, above 150° C., indicated the formation of slightly more of the 2,3-isomer at the expense of the 1,2-isomer. In all cases both anthraquinones were found. Practically theoretical yields were obtained under the following conditions: temperature, 135° C.; time, 7.5 hours; and a ratio of 8 parts of 95 per cent sulfuric acid to one part of keto acid.

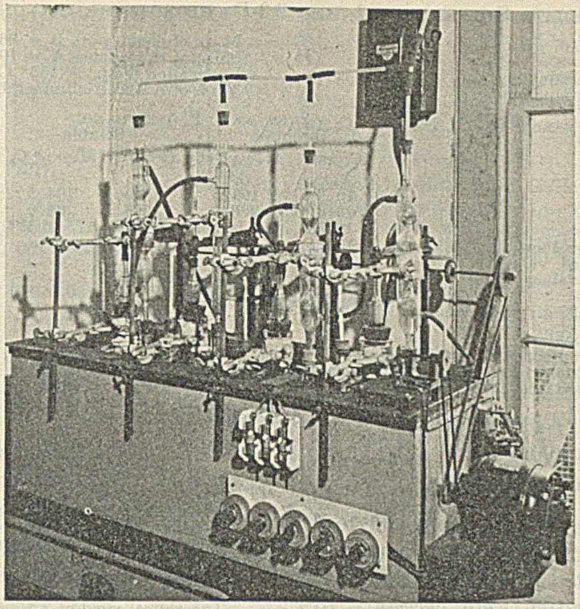


FIGURE 1. EQUIPMENT USED IN EXPERIMENTS

TABLE II. EFFECT OF TIME ON PREPARATION OF 3′,4′-DICHLORO-2-BENZOYLBENZOIC ACID

Phthalic anhydride, 0.5 mole = 74.0 grams
Anhydrous $AlCl_3$, 1 mole + 10% = 147.8 grams
1,2-Dichlorobenzene = 441 grams (3 moles)
Theoretical yield = 147.5 grams
Reaction temp. = 90° C.
M. p. of pure keto acid = 192.5° C.
M. p. of crude keto acid, all runs = 190–191° C.

Initial homogeneity obtained by manual agitation, after which there was no further stirring.

EXPT.	TIME	YIELD	
	Hours	*Grams*	*% of theory*
1	4	69.4	47.0
2	6	91.5	62.1
3	8	99.0	67.1
4	9	99.8	67.7
5	10	99.1	67.2
6	12	99.5	67.5
7	48	98.7	67.0

TABLE III. EFFECT OF TEMPERATURE ON PREPARATION OF 3′,4′-DICHLORO-2-BENZOYLBENZOIC ACID

Phthalic anhydride, 0.5 mole = 74.0 grams
Anhydrous $AlCl_3$, 1 mole + 10% = 147.8 grams
1,2-Dichlorobenzene = 441 grams (3 moles)
Theoretical yield = 147.5 grams
Reaction time = 8 hours
M. p. of pure keto acid = 192.5° G.
M. p. of crude keto acid, all runs = 190–191° C.

EXPT.	TEMP.	TYPE OF AGITATION	YIELD	
	° C.		*Grams*	*% of theory*
1	50	None	Trace	..
2	85	None	87.0	59.0
3	90	None	99.0	67.1
4	95	None	103.3	70.0
5	100[a]	None	107.5	72.9
1-A	50	Continuous	17.3	11.7
2-A	70	Continuous	50.9	34.5
3-A	85	Continuous	98.9	67.0
4-A	90	Continuous	104.5	71.8
5-A	95	Continuous	112.8	76.5
6-A	97.5	Continuous	118.0	80.0

[a] Above 100° C. the yield was not increased.

The data relating to the separation of the isomers, when this was accomplished by diluting the reaction mass to various residual acidities, are shown in Table IV. These results indicate that practically pure 2,3-dichloroanthraquinone may be obtained directly from the cyclization mixture, consisting of 92 per cent sulfuric acid, with a net yield of 82.5 per cent of 2,3-dichloroanthraquinone. With a residual acidity of 89.75 per cent sulfuric acid, a less pure 2,3-derivative of 87 per cent yield was isolated. The pure 1,2-dichloroanthraquinone could not be isolated in the manner described above. One recrystallization of the product from the filtrate of experiment 7, Table IV, from ethanol, yielded 1,2-dichloroanthraquinone with a melting point of 193° to 194° C.

Repeated recrystallizations from toluene, glacial acetic acid, or ethanol (in any order) gave in all cases the following melting points (corrected): for 1,2-dichloroanthraquinone, 194.5° C.; for 2,3-dichloroanthraquinone, 268.0° C.

TABLE IV. EFFECT OF RESIDUAL ACIDITY ON SEPARATION OF ISOMERIC ANTHRAQUINONES IN CYCLIZATION OF 3′,4′-DICHLORO-2-BENZOYLBENZOIC ACID

Keto acid = 100 grams
Sulfuric acid = 95%

$$\frac{\text{Grams keto acid}}{\text{Grams } H_2SO_4} = \frac{1}{8}$$

Residual acid = 900 grams
Reaction time = 7.5 hours
Reaction temp. = 135° C.
M. p. of 1,2-dichloroanthraquinone = 194.5° C.
M. p. of 2,3-dichloroanthraquinone = 268° C.
Theoretical yield = 93.90 grams

EXPT.	RESIDUAL ACIDITY[a]	PRIMARY PRECIPITATE Yield		PRIMARY PRECIPITATE M. P.	PRODUCT FROM FILTRATE Yield		PRODUCT FROM FILTRATE M. P.
	%	*Grams*	*% of theory*	*° C.*	*Grams*	*% of theory*	*° C.*
1	Complete diln.	93.85	99.94	235–250	...	...	.....
2	70.00	93.60	99.68	235–250	0.70	0.74	.....
3	82.00	92.90	98.93	240–250	0.90	0.96	.....
4	83.79	92.31	98.31	240–255	1.38	1.47	142–150
5	86.25	90.30	96.16	245–258	3.63	3.86	145–150
6	88.92	84.00	89.45	258–261	9.93	10.57	160–165
7	89.75	81.74	87.05	262–264	12.10	12.89	180–182
8	92.05	77.50	82.53	265–267	16.39	17.46	160–165
9	95.00	71.65	76.30	266–268	22.21	23.65	158–165

[a] It was found that changes in temperature, time, humidity, and the amount of surface of the concentrated sulfuric acid exposed affected the quantity of water absorbed. Cyclization mixtures and controls containing only concentrated sulfuric acid, run simultaneously, showed the same increase in weight. The above residual acidities were calculated by means of the following formula:

$$\frac{\text{Grams of } H_2SO_4 \text{ in cyclization acid} + \text{grams of } H_2SO_4 \text{ in diluting acid}}{A + B + C + D} = \text{Residual acidity}$$

where A = sulfuric acid used, grams
B = water absorbed, grams
C = water in diluting acid added, grams
D = water liberated by keto acid in cyclization, grams

In suitable solvents it was found that, as the temperature was elevated, the 1,2-isomer increased in solubility more rapidly than did the 2,3-dichloroanthraquinone, but in all instances the solubility at room temperature of these substances was approximately of the same degree. Table V presents data on a study of the solubilities of 1,2-dichloroanthraquinone, 2,3-dichloroanthraquinone, and various mixtures of both in ethanol. These data confirm those of Table IV, indicating that the quantitative relationship between the isomeric dichloroanthraquinones as a result of cyclization in sulfuric acid is approximately 13 per cent of 1,2-dichloroanthraquinone to 87 per cent of 2,3-dichloroanthraquinone.

Table V. Solubility Studies of 1,2- and 2,3-Dichloroanthraquinones in Ethanol

Anthraquinones = 16.67 grams
Ethanol = 1000 cc.
A = 1,2-dichloroanthraquinone
B = 2,3-dichloroanthraquinone

M. p. of chem. pure B = 268.0° C.
M. p. of chem. pure A = 194.5° C.
Cyclization temp. = 135° C.
Mixt. of A and B obtained by complete dilution

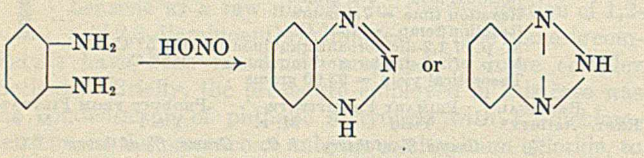
Dichloroanthraquinones	Sepn. at B. P. of Ethanol: Insoluble		Soluble		Separation at 22° C.: Insoluble		Soluble	
	Grams	M. p., ° C.	Grams	M. p., ° C.	Grams	M. p., ° C.	Grams	M. p., ° C.
	(1)[a]	(2)	(3)	(4)	(5)	(6)	(7)	(8)
M. p. = 194.5° C.; A; detd. values	12.38	194.5	4.29	194.5	3.80	194.5	0.49	194.5
M. p. = 268° C.; B; detd. values	15.61	268.0	1.06	268.0	0.63	268.0	0.43	268.0
Mixt. of A and B; detd. values	13.52	267 to 268	3.15	175 to 184	2.22	181 to 190	0.93	170 to 200
Synthetic mixt.; A = 15, B = 85%; calcd. values	13.11	.....	3.56	.....	2.64	.....	0.92	.....
Synthetic mixt.; A = 12.5, B = 87.5%; calcd. values	13.53	.....	3.14	.....	2.22	.....	0.92	.....
Synthetic mixt.; A = 10, B = 90%; calcd. values	13.94	.....	2.73	.....	1.81	.....	0.92	.....
Mixt. of A and B; 34.29 g.; detd. values	28.94	266 to 268	5.35	180 to 191	4.42	189 to 195	0.93	168 to 201
Synthetic mixt.; A = 12.5, B = 87.5%; 34.29 g.; calcd. values	28.94	.....	5.35	.....	4.43	.....	0.92	.....

[a] (1) Grams insoluble determined by weighing.
(3) Grams in solution = grams anthraquinones minus (1).
(4) An aliquot part of (3) evaporated to dryness and the melting point determined.
(5) (3) cooled to 22° C.; precipitate separated, dried, and weighed.
(7) Grams soluble = (3) minus (5).
(8) An aliquot part of (7) evaporated to dryness and the melting point determined.

Amination of Isomeric Dichloroanthraquinones

Preliminary experiments in the amination of the mixture of 1,2- and 2,3-dichloroanthraquinones indicated that more drastic conditions than those reported by Groggins and Stirton (*4*) for the monohalogen derivative were necessary to replace the second halogen. In order (1) to ascertain the susceptibility of each of the isomers to amination, (2) to avoid the formation of impurities because of differences in reactivity which might lead to condensation products, and (3) to obtain the amination products in the highest state of purity, emphasis was laid upon the amination of the purified compounds rather than on the mixture of the isomers.

The purity of diaminoanthraquinones could not be determined by the usual titration method with nitrous acid. Ladenburg (*5*) found that nitrous acid reacting on *o*-phenylenediamine yielded aminoazophenylene:



Titrations of purified *o*-diaminoanthraquinones gave approximately 50 per cent values, calculated for primary diamines. Products prepared by ammonolysis, which had shown by preliminary analysis the absence of halogen and the presence of the theoretical amount of nitrogen for an *o*-diaminoanthraquinone, behaved in the same manner.

Amination of 2,3-Dichloroanthraquinone

At an operating temperature of 200° C. it was found that a reaction time of approximately 30 hours was required to approach complete ammonolysis. Table VI presents the data obtained in a study of the effect of an oxidant, copper, and an ammonium salt, in the amination of 2,3-dichloroanthraquinone. From Table VI it is evident that all the halogen may be removed. The presence of both copper and an oxidant, under the operating conditions of the table, appears to be necessary for complete ammonolysis.

The purified 2,3-diaminoanthraquinone, in agreement with that reported in the literature (*7*), did not melt below 320° C. Scholl and Kacer (*7*) prepared 2,3-diaminoanthraquinone by reduction of the 3-nitro-2-aminoanthraquinone, from which they prepared the 2,3-diphenyl-5,6(2,3)-anthraquinonepyrazine, with a melting point of 271° C. This derivative was prepared from the diaminoanthraquinones from both sources, and it showed a melting point of 271° C. in each case and gave no depression in a mixed melting point determination. It would appear, therefore, that the principal product of ammonolysis is 2,3-diaminoanthraquinone.

Table VI. Amination of 2,3-Dichloroanthraquinone

2,3-Dichloroanthraquinone, 0.05 mole = 13.85 grams
Aqueous ammonia, 28% NH_3 = 315 grams
Reaction time = 30 hours
Reaction temp. = 200° C.
2,3-Dichloroanthraquinone, Cl = 25.60, N = 11.76%
CuO = *a*, Cu_2O = *b*
Theoretical yield of 2,3-diaminoanthraquinone = 11.90 grams

Expt.	$KClO_3$	Copper	NH_4NO_3	Yield		Cl Content	N Content
	Gram	Grams	Grams	Grams	% of theory	%	%
1	..	..	...	10.917	91.7	8.68	...
2	1.00	..	...	11.790	99.1	6.50	...
3	..	..	2.00	11.625	97.6	6.25	...
4	..	2.00*b*	...	10.116	85.0	1.83	...
5	1.00	2.50*a*	...	10.686	90.0	0.85	...
6	0.75	2.00*b*	12.00	11.323	95.2	Trace	11.69
7	0.75	2.50*a*	6.00	11.640	97.8	Absent	11.67
8	0.75	1.25*a*	6.00	11.630	97.7	Absent	11.74
9	0.75	1.25*a*	2.00	11.411	96.0	Absent	11.81

Amination of 1,2-Dichloroanthraquinone

Table VII sets forth the results of a study of the amination of the 1,2-dichloroanthraquinone. It appears that the presence of copper, an oxidant, and ammonium nitrate contributes to a satisfactory yield and purity of the 1,2-diaminoanthraquinone. Conditions stringent enough to remove both halogens favor hydrolysis, which was indicated by the isolation of hydroxyaminoanthraquinones from the ammonia mother liquor. A larger quantity of ammonium nitrate increased the yield of 1,2-diaminoanthraquinone and apparently reduced the degree of hydrolysis.

Table VII. Amination of 1,2-Dichloroanthraquinone

1,2-Dichloroanthraquinone, 0.05 mole = 13.85 grams
Aqueous ammonia, 28% NH_3 = 315 grams
Reaction temperature = 200° C.
1,2-Dichloroanthraquinone, Cl = 25.60, N = 11.76%
$KClO_3$ = 0.75 gram
Theoretical yield of 1,2-diaminoanthraquinone = 11.9 grams

Expt.	Cu_2O	NH_4NO_3	Time	Yield		Cl Content	N Content
	Grams	Grams	Hours	Grams	% of theory	%	%
1	..	2.00	20	10.640	89.40	4.05	...
2	..	2.00	25	10.527	88.46	3.44	...
3	..	2.00	30	10.056	84.50	2.75	...
4	0.50	2.00	25	10.311	86.63	Trace	10.85
5	1.00	2.00	30	10.603	89.10	Trace	11.68
6	1.00	6.00	30	10.842	91.10	Absent	11.75
7	2.00	6.00	30	11.075	93.10	Absent	11.79

By treatment of the above-mentioned diaminoanthraquinone with alizarin (*1*) dissolved in phenol in the presence of boric acid, an indanthrene dyestuff was obtained. Likewise, with *β*-naphthoquinone (*2*) an indanthrene dyestuff was produced. 1,2-Diaminoanthraquinone prepared by different methods undergoes identical condensations. In neither case did the 2,3-diaminoanthraquinone act similarly. The principal product in the ammonolysis discussed above appears to be 1,2-diaminoanthraquinone.

ACKNOWLEDGMENT

The equipment shown in Figure 1 was designed and constructed by R. Hellbach of the Color and Farm Waste Division of this bureau.

LITERATURE CITED

(1) Bayer, A., German Patent 170,562 (1904).
(2) Bayer, A., German Patent 178,130 (1905).
(3) Carswell, T. S., IND. ENG. CHEM., 20, 728 (1928).
(4) Groggins and Stirton, *Ibid.*, 25, 48 (1933).
(5) Ladenburg, A., *Ber.*, 9, 1524 (1876).
(6) Phillips, M., *J. Am. Chem. Soc.*, 49, 474 (1927).
(7) Scholl and Kacer, *Ber.*, 37, 4531 (1904).
(8) Senn, E., Dissertation, Zurich, 1923.
(9) Tanaka, M., and Tanaka, N., *Bull. Chem. Soc. Japan*, 3, 286 (1928).

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Colored Waterproof Drawing Inks

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A method for preparing a set of water-fast drawing inks is described. The inks consist of a 5 per cent solution of shellac and a suitable dye. The shellac is held in solution by ammonium hydroxide and a small amount of borax. Seven dyes, each of a different color, selected from a list of ninety-two as the most suitable for making water-fast inks, are listed. Methods of testing water-fast inks are outlined.

THE object of the experiments described was to prepare a number of representative clear water-fast inks of the dissolved dye type which would not deteriorate on storage over a period of at least one year.

The chief constituents of a water-fast ink are shellac and a suitable dye. The shellac is held in an aqueous solution with a weak base or an alkaline salt, such as borax. In an ink made by the procedure outlined later, ammonium hydroxide is depended upon to keep the shellac in solution. However, a small amount of borax is necessary to make the shellac insoluble when the ink dries. In the course of this work it was found that unbleached shellac could be used because the amount of natural dye in the shellac is not great enough to alter the shade or hue of the finished ink. Consequently no attempt was made to use bleached shellac in the work here described. The impurities, such as insoluble waxes, orpiment, and dirt, were removed from the orange shellac.

Apparently the more important of the two constituents is the dye. Of ninety-two dyes tried, only seventeen were of sufficient promise to justify using them in inks to be kept in storage for a year or more. The other seventy-five dyes were unsatisfactory because they were not soluble enough, they did not produce a water-fast ink, or their color lacked the desired purity. At the end of a year, seven of these dyes representing different colors were selected as the best for making water-fast drawing inks. Inks prepared with these seven dyes did not change color or deteriorate in any way during the aging period. At the end of two years, these inks were still good. They bled very little, if any, when subjected to the most drastic water-fastness test both before and after aging. The dyes which were found to be suitable for the preparation of colored water-fast inks are given in Tables I and II.

PREPARATION OF A WATER-FAST INK

A shellac solution was prepared by carefully digesting on a steam bath about 65 grams of orange shellac in 500 ml. of a solution containing one volume of ammonium hydroxide (specific gravity 0.90) mixed with 4 volumes of water. When the shellac had completely dissolved, the solution was allowed to cool. The waxes present were removed by repeated extraction with a mixture of equal volumes of ethyl ether and petroleum ether. Each extraction required about 3 hours to obtain a complete separation. Four such extractions were made, using about 100 ml. of the mixed ethers each time. After the last extraction the shellac solution was heated on the steam bath for 2 hours in order to eliminate all traces of the ethers. The shellac content of the cooled solution was determined, 5 ml. of ammonium hydroxide were added to insure an excess of this constituent, and the solution was diluted with water until the shellac content was reduced to 50 grams in 500 ml. One gram of phenol and 3 grams of borax were added, and the solution was vigorously shaken until these materials were dissolved.

The stock solution thus prepared was used in making the samples of ink. Convenient batches of the ink were made by mixing 50 ml. of the stock solution with 50 ml. of an aqueous solution of the dye. The ink was then filtered to remove any insoluble material introduced by the dye.

TABLE I. DYES SUITABLE FOR COLORED WATERPROOF DRAWING INK

DYE	COLOR	COLOUR INDEX NO.	SCHULTZ NO.	DYE IN 100 ML. OF INK
				Gram
Erythrosine Yellowish	Red	772	591	0.5
Brilliant Orange R	Orange	78	79	0.6
Chloramine Yellow	Yellow	814	617	0.4
Brilliant Milling Green B	Green	667	503	1.2
Wool Blue G Extra	Blue	736	565	0.5
Methyl Violet B	Violet	680	515	0.5
Benzamine Brown 3GO	Brown	596	476	0.8

TABLE II. DYES CHOSEN FOR PRELIMINARY SAMPLES OF INK BUT ELIMINATED IN FINAL SELECTION

DYE	COLOR	COLOUR INDEX NO.	SCHULTZ NO.	DYE IN 100 ML. OF INK
				Gram
Benzo Fast Orange S	Red	326	279	0.8
Benzo Fast Orange S	Red	326	279	0.3
Brilliant Croceine M		252	227	0.3
Orange R	Orange	161	151	0.4
Thiazol Yellow	Yellow	813	198	0.8
Metanil Yellow	Yellow	138	134	0.8
New Methylene Blue N	Blue	927	663	0.4
Crystal Violet	Violet	681	516	0.4
Benzo Brown G	Brown	606	485	0.6

The seven dyes of the first choice, each of a different color, together with the quantities necessary for the preparation of the batches of ink are given in Table I. The dyes listed in Table II are of second choice. Inks prepared with these dyes are not quite as fast to water as those in Table I. In preparing any of these inks, the concentrated form of the dye is desirable to prevent introducing unnecessary materials into the inks. The figures in the tables indicating the amount of dye used are only approximate because different manufacturers may furnish dyes that are identical except for their tinctorial power. At the end of two years, all of the inks in both tables were in good condition except one of the bottles of violet ink containing crystal violet. A heavy growth of mold had destroyed the color of this sample, but the other sample containing the same ink was not affected.

METHODS OF TESTING

Methods of testing water-fast inks were developed as the work progressed. At first, lines were drawn with a ruling pen on bond paper and allowed to dry for 2 or 3 hours before they were immersed in tap water for 15 minutes. As better inks were prepared, a more drastic test became necessary. This latter consisted in placing the paper, marked with the ink to be tested, between pieces of glass held in running water. As soon as the paper was in place, the two pieces of glass were pressed together to remove excess water and set aside for one hour. If the dye bled, it discolored the paper adjacent to the streaks, and the amount of bleeding was judged by the area of paper discolored. To supplement this test, strips of the paper were soaked for one hour in 200 ml. of water which was stirred occasionally. The amount of bleeding was determined by the decrease in the intensity of color of the streaks. This test was not as sensitive as the one in which glass plates were used, but it showed whether or not the bleeding noticeably affected the intensity of color.

The most drastic test was made by marking a dry paper strip with the ink to be tested, covering with a moistened filter paper, and placing the two between dry glass plates. Any dye that bled from the streak was absorbed by the filter paper. This test is a very convenient one for judging the relative merits of two or more inks.

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Blue Dye as Evidence of the Age of Writing

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Contrary to statements made by experts on disputed documents that the blue dye in writing done with ordinary blue-black ink will all be oxidized away in 15 years, examination of 147 samples of writing older than 15 years showed that blue dye was to be found in 78 of them. The oldest samples in which dye was detected were written in 1881.

It is not possible to conclude from the presence or absence of dye that one sample of writing is more recent or older than another.

ORDINARY blue-black writing ink is essentially an aqueous solution containing ferrous sulfate, tannic and gallic acids from nutgalls, free mineral acid to delay the deposition of ferric gallotannate as the ink oxidizes, and an antiseptic. Freshly made ink of this kind makes such pale marks on paper that it is customary to add also a dye, usually blue, to give an immediate color. On paper, the writing is at first blue but becomes darker and darker until it is finally black if the ink contains enough iron and tannin. The change in color is due to the formation of ferric gallotannate, whose black color hides the blue of the dye more or less completely.

The oxidation that causes the blackening does not cease when all the ferrous iron is converted into ferric, but proceeds at a rate that depends upon the conditions under which the writing is kept. In the dark the writing will last a great deal longer than if it is exposed to bright light. In either case it is only a matter of time until the organic portion of the writing is destroyed by oxidation so that only rusty marks are left, but, before this end is reached, the writing goes through a series of color changes. It is not necessary to describe these changes, for the point of present interest is the disappearance of the blue dye, which is destroyed before the black iron gallotannate becomes seriously affected. According to Mitchell and Hepworth (*2*), "the black iron tannate is much more stable to atmospheric influences than the dyestuffs used as provisional pigments, whereas the latter usually offer greater resistance to chemical agents." The chemical agent they seem to have had in mind is a 5 per cent solution of oxalic acid. On the same page they describe the results obtained by treating a number of bank checks of different ages with this solution. This reagent bleached the ferric compound, while the dye dissolved in the acid solution. They found that there "was very little diffusion [of dye] in those [checks] written five years; while after six years the reaction became very slow and there were hardly any signs of diffusion of the blue pigment. On the checks twelve years old the ink was unaffected for a long period by the reagent." And on the following page: "In abnormal cases, where an excessive amount of ink had been used, some diffusion of the blue pigment may occur even after the lapse of twelve years."

The present writer does not doubt the truth of these statements about this particular set of checks but objects to categorical claims that the blue dye must perforce disappear within a given number of years. In the examination of three letters, involved in a legal controversy, to find out the kind of ink that had been used, it was found and reported that the writing still contained enough blue dye to produce a stain on moist filter paper. The age of the letters was an important point at issue, and two handwriting experts immediately deposed that the letters could not be 15 years old because the dye had not all disappeared.

In the meantime twenty-two samples of writing on dated pages of the writer's laboratory notebooks at the Bureau of Standards had been examined (*1*). The tests were made in the summer of 1932, on writing from April, 1905, to July, 1910, all well above 15 years old. In each of the years except 1906 and 1909 one or more bits of writing gave a total of nine positive tests for blue dye. Since then many more samples of known age have been examined, and are here reported. Blue dye may last a great deal longer than 15 years, and the absence of dye in a given sample of writing does not necessarily prove that it is older than another sample in which there is a comparative abundance of dye. In other words, the presence or absence of dye in detectable amount is not a safe criterion of the age of writing. Blue-black writing ink is not a substance of definite and fixed composition. The manufacturer may vary the amounts of the iron, tannin, and acid over a considerable range to suit his own ideas, and he has a limited choice of suitable dyes which he can add to the ink in greater or smaller quantity. The amount of ink taken up by the paper depends upon the fluidity of the ink, the pen, the kind of paper, and upon the writer, who may or may not use a blotter. All these variables, in addition to the conditions under which the writing is kept, play their part in the persistence or disappearance of the dye.

Tests on Samples of Dated Writing

The only reagent used in examining the samples of writing was distilled water. A small drop was placed upon a marked letter and, after 10 seconds, was removed by pressing down upon it a piece of white filter paper. The pressure of the finger tip was maintained for 10 seconds, after which the paper was examined for blue stains. To avoid getting press copies of the blue lines ruled on some of the paper, the letter selected for the test was usually midway between two lines.

The writing examined consisted: (1) of the writer's laboratory notebooks at the Bureau of Standards, dated from October, 1904, to June, 1918; second, his lecture notes from October, 1895, to April, 1896; and third, names written in a few books and writing on a number of legal documents. There can be no serious doubt concerning the dates of any of the samples of writing. The older writing, in 1851, 1852, 1865, 1872, and 1874, seems to have been done with the old-style muddy ink that was allowed to become oxidized before it was used. These made rusty stains on the filter paper and, because of their dates, may never have contained any blue dye. The rest of the writing was done with ink from many different bottles.

Table I. Bleeding of Blue Dye from Moistened Writing When Pressed with Filter Paper

Year	Tests	Character of Stain[a]	Year	Tests	Character of Stain[a]
1851	1	Rusty	1905	12	9N, 2?, T
1852	1	Rusty	1906	6	6N
1865	1	Faintly rusty	1907	10	3F, 7D
1872	1	Strongly rusty	1908	11	?, 6T, F, 2D, S
1874	1	Faintly rusty	1909	8	6N, ?, T
1879	2	2N	1910	20	12N, ?, 3T, F, 3S
1881	2	F, D	1911	2	2D
1883	1	N	1912	2	D, S
1886	2	T, D	1913	2	2F
1895	5	T, 4F	1914	2	D, S
1896	7	5F, D, S	1915	2	2S
1901	2	2N	1916	2	2F
1903	3	F, 2D	1917	2	2N
1904	2	2N	1918	4	4N

Total, 116; no stain or doubtful, 56; positive, 60.

[a] N, none; ?, doubtful; T, trace; F, faint; D, distinct; S, strong.

The general appearance of a page of writing gave no clue to its age in comparison with other pages of the same kind. For instance, writing on the oldest pages (1904) of the laboratory notebooks looks blacker than that on other pages several years more recent. On every page there were great differences in the blackness of the writing, and accordingly a very black and a medium dark character were tested. The same was done in testing the lecture notes and two or three of the documents.

In Table I, which summarizes the results of the tests, the approximate intensities of the blue stains on the filter paper are indicated. No properly completed tests are omitted, except a few special ones that are described further on.

A few samples of writing gave such strong stains that they were further tested, not by first wetting them, but by simply pressing damp filter paper against them for 10 seconds. Of three deep black samples dated 1907, one gave a strong and two others distinct stains. Of two dated 1896, one was only medium dark, yet both gave distinct stains.

Finally, tests were made to find out whether any of the writing contained enough blue dye to diffuse out into a drop of water. A small drop of water was allowed to stand on the selected character for one minute. In most cases this character was deep black. In all, thirty-one samples were tested in this way, and the results are shown in Table II.

Table II. Bleeding of Blue Dye into Drop of Water

Year	Tests	Character of Bleeding[a]	Year	Tests	Character of Bleeding[a]
1881	2	2T	1903	2	2F
1886	4	T, F, D, S	1907	6	3N, 3F
1895	6	6N	1910	2	2S, both in 25 sec.
1896	8	4N, T, F, 2D	1911	1	D, in 30 sec.

Total, 31; no bleeding, 13; positive, 18.

[a] N, none; ?, doubtful; T, trace; F, faint; D, distinct; S, strong.

In addition to the tests of Table I, three pages of writing in the laboratory notebooks call for special comment. Four tests were made on a page dated 1907, two on line 5, one on line 8, and one on line 11. The last gave a distinct blue stain, but the other three none at all. A single line of writing in 1908, in four tests, gave three blue stains rated as trace and one that was distinct. Finally, on a page written in 1910, two tests on line 1 and one on line 4 showed no blue dye, but one on line 7 and two letters on line 13 gave strong stains. No doubt further search would have revealed a number of similar cases.

The results described in this paper, in addition to those already published (*1*), show that the presence or absence of blue dye in writing is not to be regarded as evidence of its age, whether recent or old. Certainly it is not true that writing 15 years old no longer contains blue dye. Because one of two samples of writing dated 1881 gave a distinct blue stain, and not merely a trace, it seems not improbable that somewhere there are documents even older than 52 years in which dye might be detected.

Literature Cited

(1) Anonymous, Bur. Standards, *Circ.* 400 (1933).
(2) Mitchell, C. A., and Hepworth, T. C., "Inks: Their Composition and Manufacture," 3rd ed., p. 181, Griffin & Co., London, 1924.

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Employment in the Chemical Industry in July, 1933

Index numbers showing the trend of employment and pay rolls in manufacturing industries are computed monthly by the U. S. Bureau of Labor Statistics from reports supplied by representative establishments in the principal manufacturing industries and covering the pay period ending nearest the fifteenth of the month. These figures show the percentage represented by the number of employees on weekly pay rolls in any month compared with employment and pay rolls in a selected base period. The year 1926 is taken as the index base year, and the average of the 12 monthly indexes in that year is represented by 100 per cent. Figures for the chemical industry follow:

Index Numbers of Employment and Pay-Roll Totals in Chemical Industry

(12-month average 1926 = 100)

Manufacturing Industry	Employment			Pay-Roll Totals		
	1932	1933		1932	1933	
	July	June	July	July	June	July
Chemicals and allied products	68.0	78.8	83.1	56.5	64.4	67.2
Chemicals	82.1	94.3	103.0	58.6	69.1	75.5
Cottonseed, oil, cake, and meal	28.1	27.9	31.4	28.3	27.7	30.9
Druggists' preparations	66.1	67.0	69.9	64.2	66.1	66.6
Explosives	66.6	75.4	83.3	42.8	51.2	58.5
Fertilizers	30.4	44.3	46.5	24.0	27.9	29.8
Paints and varnishes	68.9	76.4	78.7	53.0	62.3	61.5
Petroleum refining	64.1	64.7	64.7	56.8	54.6	54.5
Rayon and allied products	92.9	154.9	167.6	71.2	130.1	140.1
Soap	93.1	99.5	101.5	82.6	83.2	84.9

Butyric Acid and Butyl Alcohol Fermentation of Hemicellulose- and Starch-Rich Materials

Selman A. Waksman and David Kirsh, New Jersey Agricultural Experiment Station, New Brunswick, N. J.

A group of bacteria, capable of fermenting the hemicelluloses and the starch of various plant materials, is isolated from the soil. The acids and alcohols produced in the fermentation of these materials consist principally of butyric acid and butyl alcohol. Wheat middlings give a good yield of fermentation products, while corn meal is not readily fermented. The addition of concentrated corn steep liquor exerts a markedly favorable effect on the fermentation processes, especially in the case of the corn meal, where a good yield of butyl alcohol is obtained. Other plant products and plant materials, such as molasses, alfalfa, and corncobs support good growth of the organisms, but the fermentation process is not particularly vigorous. Purified hemicelluloses are not fermented; in the process of separation and purification, they are rendered resistant to decomposition by these organisms.

IN THE study of decomposition of hemicelluloses by microörganisms (*14*), there was isolated from the soil a group of anaërobic bacteria, belonging to the *Clostridium butyricum* Prazmowski group, and capable of utilizing hemicellulose-rich materials; in this process some of the hemicelluloses and starch, as well as certain sugars, were converted into organic acids and alcohols. Several cultures belonging to this group of bacteria were isolated and cultivated; they were found to represent a number of strains which were similar in their morphological appearance but which varied considerably in their fermentation capacity and in their ability to produce acids and alcohols from carbohydrates. They were found to be closely related to the butyric acid bacteria, but were distinguished from the typical representatives of this group by the fact that they grew not only upon sugars and starch but also upon certain hemicelluloses.

A detailed review of the literature of the bacteria forming butyric acid and butyl alcohol is found in the work of McCoy, Fred, et al. (*8*). The investigations on the anaërobic decomposition of pectins, especially in connection with the anaërobic retting of flax, and of starches and cellulose have an important and direct bearing upon the problem under consideration. Beginning with the work of Winogradsky and Fribes (*19*) and Beijerinck (*1*) and ending with that of Carbone (*2*), Makrinov (*7*), and Ruschmann (*12*), an extensive literature has accumulated on the role of bacteria in the retting process. A number of organisms, all of which belong to the butyric acid bacteria, was described; they varied in the nature of the carbohydrates attacked and in the relative amount of butyric and other acids, as well as alcohols, produced in the fermentation process. These organisms could not attack cellulose; some, however, acted upon various hemicelluloses and starches. There is no doubt that certain organisms, probably related to this group, are also capable of fermenting true cellulose (*6*).

Fermentation of Wheat Middlings

The specific problem under consideration deals with the production of organic acids and alcohols by pure cultures of anaërobic bacteria isolated from soil, using as a substrate material rich in starch and in hemicellulose. The methods of isolation and cultivation of the organisms were those commonly employed in the study of anaërobic bacteria. Wheat middlings were employed as a basic medium for the growth of these organisms. The proximate analysis of this was as follows:

	%
Moisture	11.14
Total nitrogen	2.56
Ash	3.79
Starch	16.72
Hemicelluloses	34.66

The term "hemicellulose" is commonly employed in the literature in a very loose manner. It is used here to designate those carbohydrates which are readily hydrolyzed by hot dilute mineral acids (2 per cent hydrochloric) and converted into reducing sugars, with the exception of starch, glycogen, and inulin. Some of the hemicelluloses are pure polysaccharides, while others contain uronic acid groups, like the pectins, and can be spoken of as polyuronides (*9*).

The media used for the growth of the bacteria and for the production of the organic acids were prepared by placing definite 4 to 5 per cent quantities of middlings, about 1 per cent calcium carbonate, and tap water in a series of flasks of varying dimensions. The flasks were plugged with cotton, sterilized, and inoculated with portions of a 48-hour culture of the organisms. During the growth process there developed large quantities of various gases. In some of the experiments the gases were measured quantitatively and qualitatively. A flask containing about 6 liters of medium was found to produce well over 20 liters of gas, which consisted of about 45 per cent hydrogen, the rest being carbon dioxide and a small amount of methane. The different strains of the organisms differed, however, in the composition of the gases formed in the fermentation process.

The acids produced by these organisms were both volatile and nonvolatile. In the presence of calcium carbonate only small amounts of alcohol were found in the culture; however, in the absence of the carbonate, large quantities of alcohols were formed, while the acid accumulation was reduced, a phenomenon well known in the case of the butyl alcohol fermentation process.

The analysis of the volatile acids was carried out according to the following procedure:

> At the end of the incubation period the acids were liberated by the addition of sufficient 10 per cent H_3PO_4, and the medium was filtered through cotton. An aliquot portion of the culture was steam-distilled so as to remove the volatile acids; the distillate containing the organic acids was then neutralized and concentrated, thus removing the alcohols, ketones, and other volatile products present. The acids were again liberated and determined by fractional steam distillation, at constant volume, according to the Dyer method (*4*). However, this method was found to be not fully reliable when applied to known mixtures, and an attempt was therefore made to apply the Werkman (*17*)

procedure of separation of organic acids, by means of isopropyl ether, as well as the Duclaux (*3*) method as modified by Virtanen and Pulkki (*13*).

It was found in a preliminary experiment on the influence of the incubation period upon the production of volatile acids from wheat middlings that the maximum acid production was reached, at 28° to 30° C., in 11 days; after that, the acid content of the cultures began to diminish. Further investigations brought out the fact that the various strains of the organisms did not behave alike, some producing considerable quantities of acid in a shorter time than others.

In order to determine what constituents in the middlings are utilized by the organism, a proximate analysis (*16*) was made of the solids in the culture at the beginning and at the end of the decomposition period—namely, 11 days. The results presented in Table I show that the cellulose, lignin, and protein of the medium were not attacked at all or were utilized only to a very limited extent, the residual material having a much higher relative concentration of these complexes than the original medium. The starch had nearly all disappeared, while a part of the hemicelluloses (including the pentosans) and some of the fats were decomposed by the organism. The dried residue weighed just about half of the original dry material added to the culture. The loss in weight was almost completely accounted for by the disappearance of the starch, the hemicelluloses, and the fats. The organic nitrogen present in the middlings was sufficient to supply the needs of the organism. The addition of inorganic nitrogen, in the form of ammonium salts or nitrates, did not have any favorable effect upon the growth and acid production.

TABLE I. PROXIMATE CHEMICAL COMPOSITION OF WHEAT MIDDLINGS AND OF FERMENTED RESIDUE

		FERMENTED RESIDUE			
		No $CaCO_3$		$CaCO_3$	
	TOTAL CONTROL CULTURE	Total amount left	Decomposed	Total amount left	Decomposed
	Grams	*Grams*	%	*Grams*	%
Total dry material	380	178	53.16	202	...
Ether-soluble portion	14.9	8.7	41.61	8.0	46.31
Hemicellulose and starch[a]	150	46.3	69.13	43.8	70.80
Pentosan	73	45.9	37.12	51.1	30.00
Starch	95	4.4	95.37	4.2	95.58
Cellulose	30.4	25.6	15.79	26.9	11.51
Lignin	32.6	...	...	30.9	5.21
Protein	55.1	51.8	5.99	47.6	13.61

[a] Hemicellulose figure is calculated from the reducing sugars (× 0.9) produced on hydrolysis with 2 per cent HCl for 5 hours at 100° C.; the pentosan is calculated from the furfuraldehyde yield; the starch was determined by hydrolysis with an active diastase preparation.

The alcohol production by the organisms was determined in the following manner:

An aliquot portion of the steam distillate of the culture was titrated to phenolphthalein with 0.1 *N* potassium hydroxide. A larger aliquot was then carefully neutralized, using the titration figures, and the alcohols and other volatile materials present in the culture distilled over directly; an aliquot portion of this distillate containing less than 10 mg. of alcohol was analyzed by the Dupres method, as outlined by Northrop (*10*). The alcohol was oxidized by an excess of 0.2 *N* potassium dichromate, and the excess dichromate determined by titration with potassium iodide and sodium thiosulfate. This method also accounts for the aldehydes and other reducing substances which may be present in the distillate.

The nature of the alcohol was determined by adding sufficient dichromate to the alcoholic distillate, placing in pressure flasks, and heating in a steam bath for 45 minutes in order to oxidize the alcohol to the corresponding acid; the contents were made alkaline with potassium hydroxide, and most of the liquid was distilled over. The residue was acidified with sulfuric acid and slowly distilled. The distillate was found to contain butyric acid, the odor being so strong as to make a further chemical test unnecessary. Other alcohols beside butyl may have been produced, but only in negligible quantities.

The alcohol content of the culture was found to increase with an increase in the acid content and with the advance of the period of incubation, as shown in Table II. The addition of calcium carbonate modifies considerably the relative acid and alcohol production of the organisms.

INFLUENCE OF CORN STEEP UPON FERMENTATION OF MIDDLINGS AND CORN MEAL

Corn steep liquor was found to exert a pronounced stimulating effect upon the fermentation process, as shown by the increased yield of volatile organic acids. The composition of this material was as follows:

	%
Moisture	49.16
Ash	8.76
Nitrogen	4.00

The pH of the steep was 4.5.

The influence of the corn steep upon the fermentation of middlings and corn meal is brought out in Table III. The addition of corn steep resulted in a marked increase in acid and alcohol production, both in the presence and absence of calcium carbonate.

TABLE III. INFLUENCE OF CORN STEEP ON FERMENTATION OF WHEAT MIDDLINGS[a]

CORN STEEP	$CaCO_3$	CULTURE 5				CULTURE 97			
		Volatile acid		Alcohol		Volatile acid		Alcohol	
%		*Cc. 1 N*	%[b]	*Cc. 1 N*	%	*Cc. 1 N*	%	*Cc. 1 N*	%
0	0	7.74	1.51	395.71	16.29	9.03	1.77	94.60	3.48
0.5	0	11.70	2.29	348.03	14.32	11.61	2.27	47.24	1.94
1.0	0	17.20	3.37	407.1	16.75	21.07	4.12	45.28	1.86
2.0	0	18.06	3.53	427.66	17.60	15.48[c]	3.03	64.94[c]	2.67
0	+	37.84	7.40	23.62	0.97	57.62	11.28	29.52	1.21
0.5	+	44.72	8.75	52.62	2.17	65.36	12.79	42.30	1.74
1.0	+	40.85	7.99	59.01	2.43	68.80	13.46	32.47	1.34
2.0	+	51.17	10.01	58.03	2.39	69.66	13.63	29.52	1.21

[a] The method of sterilization of the media was modified according to the following procedure: 500 cc. of water plus the solid material were placed in flasks and sterilized for 1.5 hours at 15 pounds per square inch (1.05 kg. per sq. cm.) pressure; 400 cc. sterile water were then added, and the medium was sterilized an additional 30 minutes. The flasks were inoculated with 5 cc. of a 24-hour tube culture and incubated for 6 days.

[b] Percentage of dry middlings as butyric acid and butyl alcohol.

[c] Fermentation not complete.

The nonvolatile acid fraction was next investigated. A portion of the fermented medium was subjected to steam distillation; the residue left was then made into a plaster with anhydrous sodium sulfate and extracted for 72 hours with ether in a Soxhlet extractor. The nonvolatile portion gave a positive Uffleman test in both cases, indicating the presence of lactic acid or other α-hydroxy acids.

Among the volatile acids, butyric seems to be the only important acid produced in the fermentation process. Other

TABLE II. INFLUENCE OF CALCIUM CARBONATE ON FORMATION OF BUTYRIC ACID AND BUTYL ALCOHOL FROM MIDDLINGS

(800 cc. of medium used; 100 cc. of 40 hour old inoculum of same composition as flask to be inoculated; plain medium = 5 per cent wheat middlings, $CaCO_3$ medium = 5 per cent wheat middlings + 1 per cent $CaCO_3$)

INCUBATION PERIOD	NATURE OF PRODUCT	CULTURE 5				CULTURE 97			
		PLAIN MEDIUM		$CaCO_3$ MEDIUM		PLAIN MEDIUM		$CaCO_3$ MEDIUM	
		Titration[a]	Percentage[b]	Titration	Percentage	Titration	Percentage	Titration	Percentage
Days									
1	Volatile acid	9.42	1.84	59.60	11.66	14.77	2.89	45.32	8.87
	Alcohol	202.51	8.33	137.32	5.65	121.99	5.02	131.38	5.41
3	Volatile acid	15.24	2.98	69.20	13.54	14.79	2.89	78.35	15.33
	Alcohol	203.79	8.39	195.99	8.07	95.62	3.94	92.55	3.81
5	Volatile acid	15.82	3.10	78.60	15.38	17.80	3.48	82.24	16.09
	Alcohol	274.14	11.28	188.87	7.77	186.70	7.68	116.63	4.80

[a] In terms of cubic centimeters of normal acid or alcohol.

[b] Percentage of dry middlings as butyric acid or butyl alcohol.

TABLE IV. EFFECT OF CORN STEEP ON FERMENTATION OF CORN MEAL[a]

(900 cc. of medium containing 4.5 per cent corn meal; inoculum, 5 cc. of a 24-hour culture)

INCUBATION PERIOD	CULTURE	NATURE OF PRODUCT	CORN MEAL ALONE		CORN MEAL + $CaCO_3$		CORN MEAL + CORN STEEP		CORN MEAL + CORN STEEP + $CaCO_3$	
Days			*Cc. 1 N*	%[b]	*Cc. 1 N*	%	*Cc. 1 N*	%	*Cc. 1 N*	%
3	5	Volatile acid	4.30	0.94	22.79	4.96	1.72	0.37	69.23	15.05
		Alcohol	3.14	0.14	3.14	0.14	183.92	8.41	111.40	5.09
	97	Volatile acid	2.41	0.52	16.34	3.55	4.73	1.03	54.18	11.78
		Alcohol	1.50	0.07	1.50	0.07	39.30	1.80	18.30	8.37
6	5	Volatile acid	6.88	1.50	38.27	8.32	1.72	0.37	79.12	17.20
		Alcohol	8.40	0.38	5.26	0.24	161.86	7.40	183.92	8.41
	97	Volatile acid	3.01	0.65	32.51	7.07	5.59	1.22	75.68	16.46
		Alcohol	1.50	0.07	3.60	0.16	73.94	3.38	44.54	2.04
10	5	Volatile acid	6.45	1.40	44.55	9.69	3.01	0.65	64.93	13.93
		Alcohol	9.50	0.43	15.14	0.69	277.46	12.69	151.34	6.92
	97	Volatile acid	3.44	0.75	42.14	9.16	5.16	1.12	85.14	18.51
		Alcohol	2.54	0.12	9.90	0.45	92.22	4.22	41.40	1.89
30	5	Volatile acid	9.37	2.04	64.93	14.12	5.50	1.20	72.93	15.86
		Alcohol	18.30	0.84	81.30	3.72	253.50	11.59	234.60	10.73
	97	Volatile acid	3.70	0.80	68.80	14.96	6.02	1.31	83.42	18.14
		Alcohol	5.54	0.25	96.72	4.42	138.64	6.34	107.12	4.90

[a] Corn steep = 0.5%; $CaCO_3$ = 1.0%.
[b] Percentage of dry corn meal as butyric acid and butyl alcohol.

acids were present but only in small concentration. This was further confirmed by an analysis of the volatile acids produced in the fermentation, using the procedure of Orla-Jensen (*11*) whereby the potassium salt of the acid is precipitated fractionally by silver nitrate and the silver content of the various fractions determined. The following results were obtained:

FRACTION	AG IN SALT Culture 6	AG IN SALT Culture 7	FRACTION	AG IN SALT Culture 6	AG IN SALT Culture 7
	%	%		%	%
1	55.1	55.5	5	55.3	55.6
2	55.1	55.6	6	55.4	56.1
3	55.4	55.3	7	55.3	55.7
4	55.5	55.6	8	55.5	54.2

The theoretical silver content of silver butyrate is 55.38 per cent. Butyric, therefore, appears to be the only volatile acid produced by the two organisms.

When, instead of middlings, corn meal mash was used, very little fermentation took place. In order to determine whether this was due entirely to the inability of the organisms studied to attack the starch in the corn or to a lack of certain nutrients, the effect of corn steep upon the fermentation of corn mash was studied. The medium consisted of 900 cc. of water and 4.5 per cent corn meal, some of the flasks receiving previous to sterilization 0.5 per cent corn steep, some 1 per cent calcium carbonate, and some both. The flasks were inoculated with 5-cc. portions of 24-hour cultures of two organisms (5 and 97) and placed in the incubator. At the end of definite periods of incubation, the cultures were analyzed for volatile acid and for alcohol.

The results presented in Table IV show that culture 5 is capable of producing large amounts of acid and alcohol from corn meal when corn steep is added to the medium, with and without calcium carbonate. However, the corn steep depressed acid production by culture 5 in a medium lacking a neutralizing agent, while culture 97 was stimulated. Since the corn steep was distinctly acid in reaction, this difference in behavior of the two organisms may have been due to a greater sensitivity of culture 5 to the acid conditions thus created. The differences may also have been due to the fact that culture 5 possesses a high alcohol-producing capacity, indicating the existence in this organism of a more efficient mechanism for the immediate reduction of the acids to alcohols, thus preventing their accumulation. In the presence of calcium carbonate, more active fermentation of the corn meal took place, as evidenced by the concentration of the products formed. These results further emphasize the variability of the different strains in their fermentation capacity: culture 97 produced less acid at the start of the fermentation than culture 5, but in the end overtook it. In alcohol production, however, culture 97 was always inferior to culture 5. There was a sharp increase in alcohol production in the 30 day old culture 97 (without the corn steep but with calcium carbonate) which seems to be abnormally high. No satisfactory explanation can be suggested for this.

INFLUENCE OF TYPE OF INOCULUM

A study was next made of the influence of nature of inoculum for bringing about the final fermentation. Flasks containing 900 cc. of water and 5 per cent wheat middlings were inoculated with 5 cc. of three different inocula, incubated for 5 days, and the acid and alcohol determined. The inocula were prepared as follows:

1. The plain inoculum consisted of a 24-hour culture of vegetative cells.
2. In the soil inoculum the organism was grown in a medium consisting of 100-gram portions of Sassafras sandy soil plus 2 grams of wheat middlings for 30 days; some of the soil was then used to inoculate wheat-middling culture tubes; after 24 hours of incubation these were employed for the inoculation of the large flasks.
3. In the spore inocula, 2 to 4 week old cultures were heated at 80° C. for 10 minutes to destroy the vegetative cells and the weak spores; the culture thus heated was used for inoculation purposes.

Comparatively little difference was obtained between the three different inocula; the plain vegetative cells gave somewhat lower yields of acid and alcohol. The inoculum of spores gave a higher yield, probably due to the fact that in the process of pasteurization the weak and less desirable cells were eliminated. An inoculum of this type usually shows a longer lag phase, because of the time required for the germination of the spores, but results in a more vigorous fermentation as has been pointed out by Weyer and Rettger (*18*). The soil inoculum gave results falling between the other two types; this represents a modified form of spore inoculation, since, after 30 days of growth in the soil culture, practically all of the organisms were largely in the spore state. Inoculation of a culture tube with the soil and subsequent incubation results in a fresh and vigorous vegetative culture, which can be used to inoculate the large flasks. A combination of the soil culture and pasteurization is known to be made use of in a commercial production of butyl alcohol (*5*).

FERMENTATION OF VARIOUS PLANT MATERIALS

In a search for an inexpensive plant material which might serve as a substrate for the growth of hemicellulose- and starch-fermenting organisms, the fermentation of blackstrap molasses and of alfalfa was attempted. The molasses employed had the following composition:

	%
Total nitrogen	0.78
Reducing sugars	17.25
Total sugars	49.58

It was difficult to obtain a preliminary fermentation of this material in the inoculum, which was prepared for the enrichment of the culture. The fermentation of the molasses, as shown in Table V, did not prove to be of any decided advantage over the wheat middlings, and its use was therefore discontinued.

Table V. Fermentation of Blackstrap Molasses

(6 per cent molasses + 1 per cent $CaCO_3$; 100 cc. actively fermenting inoculum used for 800 cc. of media)

Incubation Period	Volatile Acid Produced: Culture 5		Culture 97	
Days	*Cc. 1 N*	%[a]	*Cc. 1 N*	%
7	56.01	9.13	85.17	13.89
11	61.63	10.05	99.35	16.20

[a] Percentage of molasses as butyric acid.

The dried alfalfa contained 7.86 per cent hemicellulose, 12.79 per cent reducing sugar (calculated as glucose) in the hot and cold water extracts, 2.1 per cent total nitrogen, and 13.4 per cent ash. A medium was prepared containing, per flask, 74.4 grams of dry alfalfa and 800 cc. of water. After 8 days of incubation the inoculated flasks were analyzed for volatile acidity and alcohol. The results given in Table VI show that the alfalfa is fermented by both organisms, but not to a very large extent. A fair amount of alcohol was produced, however, under all conditions.

Table VI. Fermentation of Alfalfa

(800 cc. of medium, 74.4 grams dry alfalfa; corn steep, 0.5 per cent, and $CaCO_3$ 1 per cent when used; 8-day incubation)

Composition of Medium	Culture 5: Volatile acid		Alcohol		Culture 97: Volatile acid		Alcohol	
	Cc. 1 N	%[a]	*Cc. 1 N*	%	*Cc. 1 N*	%	*Cc. 1 N*	%
Alfalfa	4.73	0.56	47.88	1.19	7.74	0.92	30.16	0.75
Alfalfa + $CaCO_3$	30.10	3.56	30.16	0.75	27.95	3.31	26.32	0.66
Alfalfa + corn steep	5.16	0.61	71.74	1.79	11.61	1.37	41.72	1.04
Alfalfa + corn steep + $CaCO_3$	25.80	3.05	28.62	0.71	26.66	3.16	20.92	0.52

[a] Percentage of dry alfalfa as butyric acid or as butyl alcohol.

A similar experiment was carried through using as a source of carbohydrate ground corncobs, in concentration of 5.87 per cent. The results, reported in Table VII, show that a fair amount of volatile acidity is produced in the fermentation of untreated corncobs; however, the alcohol production was almost negligible. Culture 97 gave a much lower fermentation of the corncobs than culture 5.

Table VII. Fermentation of Corncobs

(800 cc. of medium containing 5.87 per cent ground corncobs, 0.5 per cent corn steep, 1 per cent $CaCO_3$; 8-day incubation)

Composition of Medium	Culture 5: Volatile acid		Alcohol		Culture 97: Volatile acid		Alcohol	
	Cc. 1 N	%[a]	*Cc. 1 N*	%	*Cc. 1 N*	%	*Cc. 1 N*	%
Corn cobs	4.73	0.89	1.68	0.07	4.30	0.81	1.68	0.07
Corn cobs + $CaCO_3$	19.52	3.66	1.68	0.07	11.18	2.10	1.68	0.07
Corn cobs + steep	7.74	1.45	7.84	0.31	6.45	1.21	1.68	0.07
Corn cobs + steep + $CaCO_3$	35.69	6.69	6.30	0.25	27.09	5.08	3.22	0.13

[a] Percentage of dry corn cobs as butyric acid or as butyl alcohol.

In order to determine the particular constituents of the corncobs that have undergone fermentation, liter flasks containing 45.53 grams of the dry material in 800 cc. of solution were inoculated with 5 cc. of a 24-hour culture on middlings. All the flasks had 4-gram portions of corn steep added to them (0.5 per cent concentration), and one set of the flasks received an additional 8 grams of calcium carbonate. After 11 days of incubation the flasks, to which no calcium carbonate was added, were removed and analyzed. The flasks containing the calcium carbonate were incubated for 20 days; these flasks inoculated with culture 97 failed to ferment for more than 1 or 2 days after inoculation, while the flasks inoculated with culture 5 were producing gas actively until the very end of the incubation period, thus confirming the previous observations of the greater activity of this strain.

The results presented in Table VIII show definitely that the hemicelluloses of the corncobs are attacked by the anaërobic bacteria, especially by culture 5, in the presence of calcium carbonate. The starch, which is present in the corncobs only in very small amounts, was also attacked, but did not seem to play an important role in supplying a source of energy to the organisms. The hemicelluloses of the corncobs are made up primarily of pentosans, particularly xylan. The decomposition of the pentosan was especially pronounced in the presence of calcium carbonate. The pentosan content in the decomposed residues was found to be greater than the hemicellulose obtained by the method of hydrolysis with dilute acid. This discrepancy is due to the fact that in the distillation of the pentosans with 12 per cent hydrochloric acid, not only the pentosans, but also the uronic acid complexes which do not give very much reducing sugar on hydrolysis with 2 per cent hydrochloric acid, are converted to furfuraldehyde.

Table VIII. Composition of Corncobs at Beginning and End of Fermentation by Cultures 5 and 97

(800 cc. of medium, 0.5 per cent corn steep in all flasks, 1 per cent $CaCO_3$, where used; no $CaCO_3$, 11-day incubation; $CaCO_3$, 20-day incubation)

	Control	Culture 5: No $CaCO_3$	Culture 5: $CaCO_3$	Culture 97: No $CaCO_3$
	Grams	*Grams*	*Grams*	*Grams*
Total residual dry material	45.530	41.500	39.200	41.800
Total solids in filtrate	2.032[a]	4.510	14.351	4.030
Ash in filtrate	0.349[a]	0.762	9.002	0.710
Hemicelluloses	16.432	14.025	9.967	14.446
Pentosans	15.990	14.865	10.451	15.401
Starch	0.850	0.402	0.476	0.658
Nitrogen	0.151[b]	0.241	0.187	0.202
Ash in residue	0.633	0.212	2.234	0.213
Volatile acid produced, cc. 1 N[c]		8.64	46.78	8.64
Alcohol produced, cc. 1 N[d]		3.40	9.00	4.10

[a] From corn steep.

[b] Nitrogen in corn steep = 0.160 gram.

[c] The corresponding amounts (in per cent) of dry corncobs fermented, as butyric acid, are 1.67, 9.05, and 1.67.

[d] The corresponding amounts (in per cent) of dry corncobs fermented, as butyl alcohol, are 0.14, 0.37, and 0.17.

In measuring the hemicellulose, starch, and pentosan content of the corncobs, separate samples of the material were used for each determination. The hemicellulose fraction included the starch as well. The ash content of the fresh material plus that of the corn steep added to the culture checked well with that found in the residue plus the filtrate, in the case of the flasks free from calcium carbonate. However, the flask receiving calcium carbonate gave, for some unexplainable reason, an abnormally high ash content.

The proximate analysis of the fresh corncobs was as follows:

	%		%
Total hemicellulose[a]	36.09	Total nitrogen	0.33
Pentosan	35.12	Ash	1.39
Starch	1.87		

[a] Calculated from sugar produced on hydrolysis with 2 per cent hydrochloric acid. The low nitrogen and ash content of the corncobs are probably responsible for the marked stimulating effect of the corn steep upon the fermentation of this material, as shown in Table VII.

INFLUENCE OF NITROGEN SOURCE UPON THE FERMENTATION PROCESS

A more detailed study was then made of the nitrogen and energy requirements of the organisms bringing about the fermentation. Four different media were used; these were placed, in 200-cc. quantities, in 300-cc. Florence flasks. The media were inoculated with 5-cc. portions of a 24-hour wheat-middling culture, incubated for 7 days, and analyzed for volatile acid, alcohol, ammonia nitrogen, and residual glucose. The different media had the following composition:

Composition	Medium 1	Medium 2	Medium 3	Medium 4
	%	%	%	%
Glucose	4.0	4.0	..	..
$(NH_4)_2HPO_4$	0.25	..	..	..
Corn steep	0.25	0.25	0.25	..
Casein	..	1.0	2.0	2.0
K_2HPO_4	..	..	..	0.25
$MgSO_4$	..	..	..	0.10

Distilled water was employed in the case of the first three media, while tap water was used in the last medium. The casein was brought into solution by sodium hydroxide, and the solution adjusted back to the neutral point by dilute hydrochloric acid. All the media were adjusted to pH 7.0; the addition of the corn steep to the casein solution resulted in the formation of a precipitate of the casein, owing to the acidity of the corn steep. The flasks were sterilized in flowing steam for 30 minutes on 3 consecutive days.

Table IX. Nitrogen and Carbohydrate Utilization of Cultures 5 and 97

(200 cc. of medium, 7-day incubation)

Medium	Culture	Volatile Acid	Alcohol	Glucose Left	NH_3 Nitrogen
		Cc. 1 N	*Cc. 1 N*	*Grams*	*Mg.*
1	5	3.10	9.59	6.28	77.78
	97	2.24	4.07	6.62	78.69
	Control	..	...	7.74	85.11
2[a]	5	2.15	19.42	5.72	1.23
	97	3.23	10.35	6.57	1.83
	Control	..	...	7.74	4.89
3[b]	5	..	2.73	..	16.67
	97	..	2.82	..	18.50
	Control	..	...	..	18.50
4[b]	5	..	3.48	..	17.28
	97	..	2.92	..	16.06
	Control	..	...	..	18.50

[a] 260.6 mg. of nitrogen added as casein.
[b] 521.2 mg. of nitrogen added as casein.

Culture 97 produced in medium 1 a sluggish fermentation, while culture 5 produced a considerable amount of gas in media 1 and 2 about 4 hours after inoculation. Eight hours after inoculation, culture 5 produced in medium 2 a spongy mass floating on the surface of the liquid, and buoyed up partly by the gas produced; culture 97 brought this about several hours later. This was due to the precipitation of the casein by the acid formed by the organisms. The flasks containing media 3 and 4 gave some evidence of gas production about 8 hours after inoculation; this ceased, however, in a very short time. An examination of the results given in Table IX reveals the fact that the fermentation obtained in all four media was not very vigorous. It is evident, however, that the organisms prefer casein as a source of nitrogen to the ammonium salt.

The results obtained by the use of media 3 and 4 show that the casein cannot be used as a sole source of energy by the organisms. This was further confirmed by the failure to obtain liquefaction by either organism of gelatin stabs incubated under anaërobic conditions in a MacIntosh and Fildes jar. A slight amount of gas was evolved after inoculation; this is probably due to the fermentation of the small amount of wheat middlings carried over with the inoculum; this can also account for the small amount of alcohol produced. The ammonia nitrogen in the casein media inoculated with the organisms was lower than that of the corresponding controls, showing that, as fast as the ammonia was formed in the degradation of the casein, it was used as a source of nitrogen by the organism, in the presence of available energy.

Composition of the Gases Produced in Fermentation

As to the composition of the gases produced in the anaërobic fermentation, reference may be made to the results of a typical experiment reported in Table X. The medium used in this experiment consisted of 37.5 grams of wheat middlings, 5.0 grams corn steep, and 7.5 grams calcium carbonate in 1000 cc. of water. At various intervals samples of the gas liberated during the fermentation were removed and analyzed. The results show that during the early stages of growth the gas consisted largely of hydrogen and carbon dioxide. With advancing growth the concentration of the hydrogen diminished and that of carbon dioxide increased, owing no doubt partly to the liberation of some carbon dioxide from the carbonate by interaction with the acids produced. There was very little methane or carbon monoxide at any time during the fermentation process.

Table X. Composition of Gases Liberated in Fermentation of Wheat Middlings at Different Stages of Growth

(Gas concentration, in per cent)

Gas	Age of Culture			
	20 hrs.	26 hrs.	43 hrs.	67 hrs.
CO_2	56.3	60.3	68.2	78.8
O_2	0.9	0.6	0.8	0.8
CO	0	0	0.1	0.2
CH_4	0.7	0	0.5	0.2
H_2	41.2	38.7	27.7	18.0

Discussion

The results of the above investigations, as well as others not reported here, prove beyond any doubt that the organisms under consideration are able to bring about the decomposition under anaërobic conditions or the fermentation of a variety of carbohydrates, including sugars (glucose, lactose), starch, hemicelluloses (mannan, galactan), but not of cellulose or of lignin. The most important point to be established by these investigations is the ability of certain anaërobic bacteria to utilize various hemicelluloses and produce acids and alcohols. It was essential to use plant materials rich in one or more specific hemicellulose, as shown for the pentosans in the experiment on the fermentation of corncobs. When Irish moss was used as the substrate, culture 5 decomposed within a few days 84.3 mg. out of 531.4 mg. of the galactan added to the culture. When salep root was used, the culture decomposed the mannan actively, producing an abundant quantity of gas. It is of interest to recall here that culture 5 was isolated from soil by the use of a mannan medium, and 97 by the use of a xylan medium.

When freshly isolated, the bacteria were much more active in bringing about the fermentation of purified hemicelluloses, as shown elsewhere (*14*, *15*). Continued cultivation in the laboratory, in pure culture, resulted in a marked deterioration of the fermentation capacity, especially when purified hemicelluloses were used as sources of energy. No attempt was made to study this phenomenon in detail. There is no doubt, however, that the vigor of the strains can be reëstablished by proper methods of cultivation and selection.

Summary

The acid- and alcohol-forming capacity of a series of anaërobic bacteria isolated from soil and capable of fermenting hemicelluloses and starch was studied. Two organisms were selected for most of the investigations reported here. Both forms produced large amounts of butyric acid and smaller concentrations of nonvolatile acid, containing some lactic. One of the cultures produced a typical butyl alcohol fermentation. Corn meal was not fermented readily, but the addition of corn steep had a markedly favorable effect upon the process of growth and fermentation. Wheat middlings were found to give the best medium for both growth and fermentation; the addition of corn meal to this medium did not exert any favorable effect, while the addition of corn steep did.

The addition of calcium carbonate to the medium resulted in the suppression of alcohol production and in an increase in volatile acidity.

Molasses, alfalfa, corncobs, and certain other plant products can be used as a medium for the growth of these organisms, but the extent of fermentation was found to be parallel to the amount of available carbohydrate.

Although the organisms were able to utilize pentosans in the form of corncobs, mannans in the form of salep root, and galactan in the form of Irish moss, very little growth was produced on the purified hemicelluloses.

Casein and ammonium salts can be utilized as sources of nitrogen, the former being preferred.

Acknowledgment

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Literature Cited

(1) Beijerinck, M. W., and Delden, A. van, *Arch. Sci. Ex. Nat. Neerl.*, (II) **9**, 418–41 (1904).
(2) Carbone, D., and Tobler, F., *Faserforschung*, **2**, 163–84 (1924).
(3) Duclaux, E., *Ann. inst. Pasteur*, **9**, 811–39 (1895).
(4) Dyer, D. C., *J. Biol. Chem.*, **28**, 445–73 (1917).
(5) Killeffer, D. H., Ind. Eng. Chem., **19**, 46–50 (1927).
(6) Langwell, H., *J. Soc. Chem. Ind.*, **51**, 988–94 (1932).
(7) Makrinov, I. A., *Ann. sci. biol.* (Petrograd), **18**, No. 5 (1915).
(8) McCoy, E., Fred, E. B., Peterson, W. H., and Hastings, E. G., *J. Infectious Diseases*, **39**, 457–83 (1926); **46**, 118–37 (1930).
(9) Norman, A. G., *Biochem. J.*, **23**, 524–35 (1929).
(10) Northrop, J. H., Ashe, L. H., and Senior, S. K., *J. Biol. Chem.*, **39**, 1–21 (1919).
(11) Orla-Jensen, S., *Centr. Bakt. Parasitenk.*, *II Abt.*, **13**, 291–306 (1903).
(12) Ruschmann, G., and Bavendamm, W., *Ibid.*, **64**, 340–94 (1925).
(13) Virtanen, A. I., and Pulkki, L., *J. Am. Chem. Soc.*, **50**, 3138–51 (1928).
(14) Waksman, S. A., and Diehm, R. A., *Soil Sci.*, **32**, 73–95 (1931).
(15) *Ibid.*, **32**, 119–39 (1931).
(16) Waksman, S. A., and Stevens, K. R., Ind. Eng. Chem., Anal. Ed., **2**, 167 (1930).
(17) Werkman, C. H., *Ibid.*, **2**, 302 (1930).
(18) Weyer, E. R., and Rettger, L. F., *J. Bact.*, **14**, 399–424 (1927).
(19) Winogradsky, S., and Fribes, V., *Compt. rend.*, **121**, 742 (1895).

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The Alchymists

by

David Teniers, the Younger

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* * *

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The Chemistry of Soft Rubber Vulcanization

I. Measurement of Vulcanization

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For a series of rubber-sulfur compounds and for four commercial, high-gum accelerated compounds the changes during cure have been measured by a series of physical tests. The change in combined sulfur has also been measured for the rubber-sulfur compounds. Experimental conditions have been so controlled that all results are comparable.

Based on the experimental results, a set of criteria has been selected with approximate limiting values for unvulcanized and for vulcanized rubber. Conditions are specified under which the criteria can be used to measure the degree of vulcanization. The selection of these criteria is, in effect, a definition in terms of the changes in physical properties which limits the meaning of the term "vulcanization" in a manner useful for the study of the phenomenon.

The difference in the rate of change of the several properties is interpreted as evidence that during vulcanization a mechanical structure is built up.

VULCANIZATION is universally recognized as a process for improving the properties of rubber for various uses, generally by treatment with sulfur or sulfur chloride. The tests made to determine the degree of vulcanization approach in multiplicity the variety in the uses of rubber.

Bruni (*2*) comments that there is still no satisfactory method of determining when rubber is vulcanized. Definitions of vulcanization such as those of Weber (*13*), Schidrowitz (*10*), Kindscher (*7*), and Shepard (*11*), all specify treatment with sulfur or sulfur-bearing compounds. Bridgwater (*1*) defines vulcanization as a change in the physical state of the rubber which is accompanied by certain changes in physical properties. In most cases no definition is given, but the coefficient of vulcanization or the change in some physical characteristic such as solubility or tensile strength is used to measure the degree of vulcanization. Thus Wiegand (*14*) considered coefficient of vulcanization, elongation at break, tensile strength, modulus, tensile product, and resilient energy in selecting optimum cure. Williams (*15*) and Dieterich and Davies (*4*) used plasticity measurements to detect scorching or incipient vulcanization.

For a study of the chemistry of vulcanization it is necessary to define what phase of vulcanization is to be considered. Such a definition can best be made in terms of the change in a specified set of physical characteristics, which should as far as possible characterize all types of vulcanization. The first step in the study is an examination of the changes brought about by curing rubber with sulfur.

The physical properties of vulcanized rubber depend on so many variables that a comparison of the results obtained at different times and in different places is unsatisfactory unless all experimental details are reported. In the present study the changes in physical properties and in combined sulfur for a series of rubber-sulfur compounds have been measured under conditions which make all of the results comparable. Physical testing data are also included for four accelerated compounds of commercial, high-gum types to show that the same changes take place in the presence of accelerators.

The choice of the test, or tests, used to measure the degree of vulcanization may materially affect the conclusions to be drawn. Thus, as judged by tensile strength alone, we might conclude from the examination of a tough crude rubber, the same rubber after milling, and the same rubber after heating with sulfur that vulcanization was exactly the reverse of milling and that the tough crude rubber was vulcanized to the same degree as the milled rubber heated with sulfur.

Experiments which will be reported elsewhere show that unmilled rubber, gas black, and stiffeners produce some effects similar to vulcanization. This makes the choice of a suitable set of tests for all types of stock rather complicated. At the present time a too comprehensive treatment seems of doubtful value. It is better to accept the necessary restrictions and to work within the limits imposed by them. In this study the limitations have been observed by establishing the following standard procedure:

The rubber is moderately masticated by following the mixing procedure of the American Chemical Society (*9*). The use of stiffeners, reclaims, and large amounts of softener or pigment, particularly gas black, is avoided. If these precautions are observed, the uncured batch stock is definitely unvulcanized by every test applied. All of the changes can then be attributed to vulcanization and dependable comparisons can be made between different types of high-gum stock.

The rubber for all the experiments reported was taken from one batch of selected, first latex crepe which was blended on an 84-inch mill in the factory. All of the batches were given as nearly the same mechanical treatment as was possible without extreme precautions. In several cases good checks were obtained in duplicate batches, which shows that the errors due to processing were insignificant.

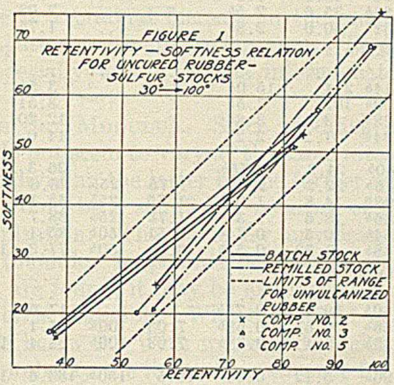
After a consideration of the theoretical and practical aspects of the problem four types of tests were selected: (1) qualitative, (2) plasticity, (3) hysteresis, and (4) stress-strain tests. Certain of the measurements have been selected as being suitable for use without the others, and in the tables these are marked ^{b}. Discussion of the tests is based on a large number of experiments, and can be verified by an examination of the data given in the tables and curves.

Qualitative Tests

Qualitative tests considered by practical rubber men to show characteristic differences between vulcanized and unvulcanized rubber are included in this work because of their relation to manufacturing operation. Testing conditions were standardized and a semi-quantitative method of classification developed so that the results are comparable to those of the other tests. Unvulcanized rubbers are put into class 0. With increasing degree of vulcanization the stocks are classified as 1, 2, 3, 4, or 5.

The tendency of stretched rubber to freeze is measured in the ice water test. When unvulcanized rubber is stretched, immersed in ice water, and released, it does not recover as it does at room temperature. This is called freezing. When stretched frozen rubber is again warmed, it recovers. This test is not sensitive during the early stages of cure. In some cases, as with high accelerator–low sulfur stocks, the rubber may seem well vulcanized by every other test and yet freeze badly in ice water. There are five classes based on this test.

The hot water test measures the tendency of stretched rubber to break by plastic flow under the influence of heat. Although unvulcanized rubber breaks readily, after only a slight cure the samples no longer break. Thus, the test can distinguish only between unvulcanized rubber and rubber which has a definite, even if slight, cure. There are two classes based on this test.



Behavior on the mill appears to give a composite measure of those changes which are most characteristic of vulcanization. The measurement, however, is not sufficiently exact to permit quantitative use. There are six classes based on the milling test.

Solubility differences in the rubber before and after milling are measured by the solubility test. The change shown here is largely complete in the early stages of cure. There are five classes based on the solubility in benzene:

Ice Water Test. In applying this test a thin strip of stock was cut from the sheet and stretched almost to the limit six times. While stretched it was immersed in ice water for 20 seconds and then released under water. Uncured rubber froze very badly and showed practically no recovery on release. With increasing cure there was more tendency to recover, and the recovery was more rapid. Finally, with the well-cured rubber the stock recovered just as rapidly in ice water as it did at room temperature. Between the two extremes were all gradations of freezing as indicated by the rate of recovery. By this test stocks can be divided into five classes from unvulcanized to well-vulcanized:

Class 0. (a) Practically no recovery
(b) Stock is too weak to test
Class 1. Some recovery, but very slow
Class 2. Recovery is faster than in class 1 but slower than in class 3
Class 3. Recovery is slower than in air
Class 4. Recovery is as fast as in air

Hot Water Test. A thin strip of rubber was cut from the sheet, stretched, and held under the hot water faucet. The water temperature was close to 90° C. The sample was kept under a tension insufficient to cause a sharp break but sufficient to cause plastic flow. The uncured stocks flowed and broke under the influence of the heat. After even a slight cure, the stocks no longer broke:

Class 0. Stock breaks or is too weak to test
Class 1. Stock does not break

Milling Test. The milling tests were carried out on a 12-inch (30.5-cm.) mixing mill (*9*). It was found that sharper differentiations could be made on a hot mill than on a cold one. Hence the mill was kept at temperatures between 90° and 110° C. The standard time for milling was 8 to 10 minutes. During most of this period the mill was kept tight [opening about $^1/_{32}$ inch (0.79 mm.) or less], but toward the end it was opened wider and the stock sheeted thicker. At this point scorched rubber shows more roughness than crude rubber. According to their behavior on the mill the stocks were divided as follows:

Class 0. Stock behaves like milled crude rubber; these stocks quickly become smooth and plastic
Class 1. Stock mills like tough crude rubber; these stocks are initially somewhat harder and rougher and take longer to break down and mill smoothly
Class 2. Stock is rather hard and dry and somewhat grainy; it usually smooths out on longer milling, especially on a cool mill
Class 3. Stock is rough and dry and does not smooth out satisfactorily
Class 4. Stock crumbles somewhat but after a few minutes hangs together well enough to form a rough sheet
Class 5. Stock crumbles very badly and does not sheet out even after 10 to 15 minutes on the mill

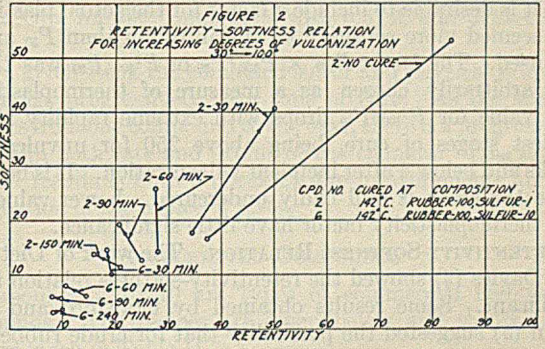
The standard procedure was modified in some cases for convenience. Thus for soft, sticky stocks a much cooler mill was used. In some cases it was necessary (for reasons not connected with the investigation) to use different mills. In many cases it was not necessary to leave the rubber on the mill for the full 10 minutes, as the classification was obvious after 3 to 5 minutes. Such variations in procedure do not affect the classification.

Solubility Test. For the solubility test sufficient compound to contain one gram of rubber was cut up into thin strips and put into 100 cc. of benzene. It was allowed to stand for 24 hours with intermittent shaking by hand. Solubility was determined both before and after the milling test. The uncured stocks were completely soluble before and after milling. With increasing times of cure, solubilities decreased, and on this basis the stocks could all be divided into five classes. The time of milling will influence solubility but within the limits used for the milling tests consistent results can be obtained:

Class	Before Milling	After Milling
0	Dissolves completely	Dissolves completely
1	Pieces lose their shape but do not dissolve completely	Dissolves completely
2	Pieces retain their shape	Dissolves completely
3	Pieces retain their shape	A few undissolved flocs are present
4	Pieces retain their shape	Stock is swollen rather than dissolved

Plasticity Tests

The retentivity and softness were measured on the Goodrich plastometer, and the plasticity was calculated from them by the procedure described by Karrer, Davies, and Dieterich (*5*). Determinations were made at both 30° and 100° C. The values are given as R_{30}, R_{100}, S_{30}, S_{100}, P_{30}, and P_{100}, with the subscripts indicating the temperature of measurement.



The heating period for the sample was 30 minutes. With the cured sheets, strips were plied to the required thickness with the help of a pure gum cement, a procedure found to give satisfactory results.

Changes in plasticity factors are greater and more abrupt at 100° than at 30° C. The major portion of all of these changes takes place in the early stages of cure, after which the change is comparatively small. As a measure of the degree of vulcanization, R_{100} was selected as the best of this group. For unvulcanized stocks it has a value consistently above 60. It is generally between 80 and 95 but is somewhat lower for lightly milled stocks. Very slight vulcanization lowers R_{100} below 60, and at 20 the stock is still very badly undercured. For well-vulcanized stocks R_{100} is below 10,

Table I. Changes during Vulcanization of Rubber with Sulfur

Cure at 142° C.[a]	Qualitative Tests				Plasticity Tests							Hysteresis Tests					Stress-Strain Tests				Coefficient of Vulcanization
	Ice water	Hot water	Milling	Solubility	R_{30}	R_{100}	S_{30}	S_{100}	P_{30}	P_{100}	$\frac{P^2_{100}}{P_{30}}$	Set	Modulus at 300%		Set/Modulus		Modulus at 500%		Ultimate tensile		
Min.													Kg./cm.^{2}	Lb./in.^{2}	Kg.	Lb.	Kg./cm.^{2}	Lb./in.^{2}	Kg./cm.^{2}	Lb./in.^{2}	
COMPOUND 2: FIRST LATEX CREPE, 100; SULFUR, 1																					
None	0	0	0	0	37.5	83.6[b]	16.6	53.1	6.2	44.4	316[b]	...	...	...	...	...	...	...	...	..	..
30	0	0	0	0	34.5	50.1[b]	17.7	40.6	6.1	20.4	68[b]	c	...	...	...	...	c	...	...	..	0.13[b]
60	0	0	0	1	28.1	27.6[b]	14.2	25.9	4.0	7.1	12.6[b]	c	...	...	...	...	c	...	1.76	25[b]	0.23[b]
90	0	0	0	1	25.0	20.7[b]	12.7	19.4	3.2	4.0	5.0[b]	220[b]	1.12	16[b]	196.3	13.7[b]	c	...	3.51	50[b]	0.33[b]
120	0	0	0	2	20.9	16.6[b]	11.7	15.6	2.4	2.6	2.8[b]	150[b]	1.41	20[b]	106.4	7.5[b]	c	...	3.51	50[b]	0.44[b]
150	0	0	0	2	21.0	16.1[b]	11.5	13.9	2.4	2.2	2.0[b]	130[b]	1.69	24[b]	76.9	5.5[b]	c	...	3.51	50[b]	0.53[b]
180	0	1	0	2	18.1	16.2[b]	10.3	13.1	1.9	2.1	2.3[b]	110[b]	1.97	28[b]	55.8	3.9[b]	c	...	10.54	150[b]	0.62[b]
210	0	1	0	2	18.7	14.4[b]	10.4	12.3	2.0	1.8	1.6[b]	105[b]	1.97	28[b]	53.3	3.75[b]	c	...	10.54	150[b]	0.67[b]
240	0	1	1	2	16.6	15.0[b]	11.0	13.2	1.8	2.0	2.2[b]	105[b]	2.10	30[b]	49.8	3.5[b]	c	...	7.03	100[b]	0.76[b]
300	0	1	1	2	15.2	14.2[b]	10.2	11.4	1.6	1.6	1.6[b]	90[b]	2.53	36[b]	35.6	2.5[b]	c	...	7.03	100[b]	0.81[b]
360	0	1	1	2	17.6	16.3[b]	10.5	13.2	1.9	2.0	2.3[b]	90[b]	2.24	32[b]	40.0	2.8[b]	c	...	1.75	25[b]	0.82[b]
COMPOUND 4: FIRST LATEX CREPE, 100; SULFUR, 3																					
None	0	0	0	0	48.9	96.2[b]	27.4	74.0	13.4	71.1	377[b]	...	...	...	...	...	...	...	...	..	..
30	0	0	0	1	29.7	33.4[b]	16.3	36.8	4.8	12.3	31.5[b]	210[b]	0.98	14[b]	214	15.0[b]	c	...	3.51	50[b]	0.25[b]
60	0	1	0	2	23.1	18.9[b]	13.4	20.1	3.1	3.8	4.6[b]	150[b]	1.40	20[b]	107	7.5[b]	c	...	3.51	50[b]	0.46[b]
90	0	1	1	2	18.8	15.2[b]	11.8	14.8	2.2	2.3	2.4[b]	105[b]	1.96	28[b]	53.6	3.8[b]	c	...	12.20	175[b]	0.68[b]
120	0	1	2	3	15.2	12.4[b]	10.5	12.4	1.6	1.5	1.4[b]	75[b]	2.39	34[b]	31.2	2.2[b]	c	...	14.0	200[b]	0.85[b]
150	1	1	3	3	14.8	13.0[b]	9.8	11.0	1.5	1.4	1.3[b]	70[b]	2.81	40[b]	24.9	1.75[b]	c	...	26.3	375[b]	1.04[b]
180	1	1	3	4	13.8	9.3[b]	9.2	9.6	1.3	0.9	0.62[b]	70[b]	3.16	45[b]	22.2	2.0[b]	1.75	25[b]	26.3	375[b]	1.30[b]
210	1	1	4	4	12.5	8.7[b]	9.3	9.0	1.2	0.8	0.54[b]	50[b]	3.37	48[b]	14.8	1.04[b]	1.75	25[b]	35.1	500[b]	1.42[b]
240	2	1	4	4	12.6	10.6[b]	8.9	9.3	1.1	1.0	0.91[b]	60[b]	3.23	46[b]	18.6	1.3[b]	1.75	25[b]	38.7	550[b]	1.60[b]
300	3	1	4	4	13.3	8.7[b]	8.5	8.3	1.1	0.7	0.45[b]	40[b]	3.80	54[b]	10.5	0.74[b]	3.51	50[b]	35.1	500[b]	2.10[b]
360	4	1	4	4	12.2	10.0[b]	7.5	7.4	0.9	0.7	0.55[b]	35[b]	4.78	68[b]	7.33	0.51[b]	3.51	50[b]	77.3	1100[b]	2.33[b]
COMPOUND 6: FIRST LATEX CREPE, 100; SULFUR, 10																					
None	0	0	0	0	38.8	88.3[b]	17.0	61.8	6.6	54.5	450[b]	...	...	...	...	...	...	...	...	...	..
30	0	0	1	2	19.4	18.5[b]	10.3	14.5	2.0	2.7	3.6[b]	110[b]	2.81	40[b]	39.1	2.75[b]	...	...	17.6	250[b]	0.55[b]
60	1	1	3	3	14.6	10.7[b]	6.4	8.1	1.0	0.9	0.8[b]	45[b]	4.21	66[b]	9.67	0.68[b]	7.03	100[b]	35.1	500[b]	1.14[b]
90	3	1	4	4	9.7	8.2[b]	5.7	6.0	0.6	0.5	0.40[b]	30[b]	5.76	82[b]	5.4	0.38[b]	7.03	100[b]	84.4	1200[b]	1.54[b]
120	4	1	5	4	8.0	4.3[b]	4.9	5.0	0.4	0.2	0.01[b]	35[b]	6.75	96[b]	5.12	0.36[b]	10.5	150[b]	133.6	1900[b]	2.40[b]
150	4	1	5	4	7.6	5.0[b]	4.6	4.5	0.3	0.2	0.01[b]	15[b]	9.12	130[b]	1.58	0.11[b]	14.1	200[b]	161.7	2300[b]	3.16[b]
180	4	1	5	4	6.1	8.6[b]	3.9	4.1	0.2	0.4	0.8[b]	20[b]	10.5	150[b]	1.85	0.13[b]	15.8	225[b]	154.7	2200[b]	3.85[b]
210	4	1	5	4	14.0	9.0[b]	4.0	3.5	0.6	0.3	0.01[b]	10[b]	12.1	172[b]	0.71	0.05[b]	24.6	350[b]	186.3	2650[b]	4.55[b]
240	4	1	5	4	8.4	10.0[b]	3.3	3.8	0.3	0.4	0.5[b]	10[b]	13.8	196[b]	0.85	0.06[b]	31.6	450[b]	207.4	2950[b]	5.27[b]

[a] 142° C. = 288° F. = 40 pounds steam pressure.

[b] Measurements suitable for use without the others.

[c] Satisfactory readings could not be made as the stock was too soft.

beyond which point further changes are comparatively insignificant.

Thermoplasticity. The fact that the plasticity values at 100° dropped much more rapidly than those at 30° C. suggested that some expression for thermoplasticity would be a useful criterion. One such expression would be P_{100}/P_{30}. However, both factors can be low and the ratio high; so that it is desirable to include a factor for the actual plasticity. P_{100} seemed more sensitive to vulcanization than P_{30} and it was used. The factor $P_{100} \times P_{100}/P_{30}$ or P^2_{100}/P_{30} was therefore arbitrarily chosen as a measure of thermoplasticity. The value for P^2_{100}/P_{30} drops with extreme rapidity in the earliest stages of cure, being above 250 for unvulcanized stocks and below 4 after incipient vulcanization. It is below 1 while the stock is still badly undercured. Lower values for this thermoplasticity factor have little significance.

Retentivity-Softness Relation. The work of Dieterich and Davies (*4*) showed the retentivity-softness relation to be significant. Some results obtained by Crawford and Bramann (*3*) suggested the possibility that for crude rubber the variation in softness and retentivity with temperature is such that they maintain a linear relationship. Vulcanization should cause considerable change in the relation. If this view is correct, the curve obtained by plotting retentivity against softness at 30° and 100° C. should be characteristic. Figure 1 shows the softness-retentivity relation for the uncured rubber-sulfur stocks.

Some variation was found both in the position and slope of the curve for milled crude rubbers. Within the area enclosed by the dotted lines, both slope and position may vary. Further milling causes a shift in the curves but does not put them outside the dotted lines. It is probable that part of this shift is due to inaccuracy of measurement on stocks of the extreme plasticity which these heavily milled stocks reach at 100° C.

The change in the retentivity-softness relation due to vulcanization is shown in Figure 2. There is a gradual shift with regard to slope, position, and length as the cure progresses. The significant change in these curves is completed in the early stages of cure. This relation is particularly useful in differentiating tough crude rubber from scorched rubber and will be discussed in that connection in a subsequent paper.

Hysteresis Tests

The hysteresis tests were run on an autographic machine built for the Goodrich testing laboratory. The rate of stretch was 20 inches (50.8 cm.) per minute. The data were obtained for 300 per cent elongation. Curves were recorded for the first, second, and fifth cycles. The area enclosed by the loops was not employed, as entirely different types of loops enclosed the same area. The significant measurements were the set and the modulus at 300 per cent elongation:

Table II. Physical Properties[a] of Technical High-Gum Stocks

Compound	Cure	Temp.	Qualitative Tests				Plasticity Tests							Hysteresis Tests					Stress-Strain Tests			
			Ice water	Hot water	Milling	Solubility	R_{30}	R_{100}	S_{30}	S_{100}	P_{30}	P_{100}	$\frac{P^2_{100}}{P_{30}}$	Set	Modulus at 300%		Set/modulus		Modulus at 500%		Ultimate tensile	
	Min.	° C.													Kg./cm.^{2}	Lb./in.^{2}	Kg.	Lb.	Kg./cm.^{2}	Lb./in.^{2}	Kg./cm.^{2}	Lb./in.^{2}
[c]	None	...	0	0	0	0	46.1	67.6[b]	15.0	31.4	7.0	21.9	68.5[b]	..	..	...	..	..	..	...	...	...
7	15	142	4	1	5	4	3.1	8.6[b]	3.9	3.4	0.12	0.29	0.7[b]	15[b]	24.6	350[b]	0.57	0.04[b]	77.3	1100[b]	236	3350[b]
8	20	127	4	1	5	4	6.5	3.4[b]	3.5	3.4	0.24	0.12	0.06[b]	10[b]	22.8	325[b]	0.43	0.03[b]	54.5	775[b]	295	4200[b]
9	20	127	4	1	5	4	3.7	5.9[b]	3.4	2.9	0.13	0.18	0.25[b]	15[b]	28.1	400[b]	0.57	0.04[b]	77.3	1100[b]	320	4550[b]
10	90	143	4	1	5	4	3.5	5.0[b]	3.5	3.5	0.12	0.18	0.27[b]	15[b]	21.8	310[b]	0.71	0.05[b]	49.2	700[b]	288	4100[b]

[a] The coefficient of vulcanization was not determined on the compounds; it was probably between 2.5 and 3.0.

[b] Measurements suitable for use without the others.

[c] Data given for only one uncured stock. It is typical for all four.

The "hysteresis set" was determined by the intersection of the fifth loop with the elongation axis. The modulus at 300 per cent elongation was taken as the highest load registered in the first loop. The measurement of modulus from the hysteresis curve is more accurate than from the stress-strain curve because of the greater sensitivity of the machine under small loads.

The test is not readily applied to mixed stocks before cure, and the results are often not significant and add very little to the information given by plasticity tests. Hence this test was not generally applied to the uncured stocks.

The value of hysteresis set for unvulcanized stocks is above 150 per cent. With only a slight degree of vulcanization it falls below 90. With well-cured rubber it is from 10 to 15. There is a gradual increase in the modulus at 300 per cent elongation, with increasing cure. These measurements are especially useful for the intermediate stages of cure.

Hysteresis Set/Modulus. Since modulus at 300 per cent and set do not seem to vary at the same rates, it seemed probable that dividing the latter by the former would give a factor which would be a significant measure of the changes due to vulcanization. The value for unvulcanized rubber is above 10 (modulus in pounds per square inch) and, if higher values are found, it may be assumed that the degree of vulcanization is negligible. With only slight vulcanization the value falls below 2. With well-cured stocks it is below 0.1, which is probably the limit of significance for this value. This factor is most useful in judging the intermediate degrees of vulcanization.

Stress-Strain Tests

Modulus at 500 Per Cent Elongation and Ultimate Tensile Strength. The stress-strain data were obtained on a standard Scott machine following the procedure adopted by the American Chemical Society (*9*) without accurate temperature and humidity control. The tensile sheets were cured in a 6 × 8 × $^3/_{32}$ inch (15.2 × 20.3 × 0.24 cm.) mold. The modulus at 500 per cent elongation and the ultimate tensile strength are the measurements used.

For the unvulcanized stocks and many of the undercured sheets the modulus at 500 per cent and tensile strength are too low to be significant. They increase very slowly in the intermediate stages of cure and become high only after the stock is rather well cured. These values are useful in the higher range of cures.

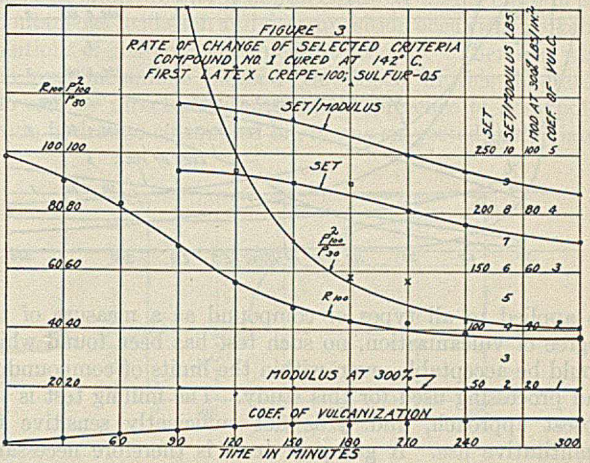
Determination of Combined Sulfur

Combined sulfur was determined directly on the sample after 48-hour acetone extraction. All results reported are the average of two check determinations. For check results the agreement was within 0.05 where the values for combined sulfur were below 1.0 per cent. Above 1.0 per cent the agreement was within 0.2, with very few exceptions being within 0.1. In this paper all results have been reported as the coefficient of vulcanization as defined by Weber (*12*). Since all recipes have been written on the basis of 100 parts by weight of rubber, this coefficient can be calculated as follows:

$$\text{Coefficient of vulcanization} = \%\ \text{combined sulfur found} \times \frac{\text{total parts in recipe}}{100}$$

Periodic determinations were made on mixed batches without cure to check the accuracy of the method. In most cases the coefficient for the uncured stocks was between 0.05 and 0.10, although it occasionally went up to 0.15. This indicates that all coefficients may be approximately 0.1 too high, owing to experimental error and sulfur in reagents. This is a constant error and, since the authors are interested primarily in comparative results, it has been considered more desirable to report results as found than to correct them for the probable error.

The correction of the coefficient of vulcanization for the acetone-insoluble sulfur combined with nonrubber constituents, as indicated by the work of Kelly (*6*), would be too small to be significant for this work.



The method of analysis selected for this work is a modification of that described by Kratz, Flower, and Coolidge (*8*) in which the extracted sample was oxidized by a mixture of bromine and fuming nitric acid.

Rubber-Sulfur Compounds

For this work 100 parts of rubber were mixed with 0.5, 1, 2, 3, 5, and 10 parts of sulfur, compound numbers 1 to 6. Sheets were cured at 142° C. (288° F.) for half-hour intervals up to 4 or 6 hours. Table I gives the complete set of data for the stocks with 1, 3, and 10 parts of sulfur. In Figures 3 to 5, coefficient of vulcanization and the physical properties selected as most significant are plotted against time of cure for the compounds with 0.5, 2, and 5 parts of sulfur.

For a given stock the combined sulfur and physical properties change progressively with time of cure. As the sulfur increases from one compound to the next, there is a progressive increase in both rate and extent of the changes. This regularity of results is both a check on the measurements and a confirmation of the choice of tests.

Accelerated Compounds

Compounds 7 to 10 are types of commercial high-gum compounds. The recipes are given below and the testing data are given in Table II.

7	
First latex crepe	100.0
Zinc oxide	5.0
Sulfur	3.0
Polybutyraldehyde aniline	0.3
Mercaptobenzothiazole	0.4
	108.7

Cure: 15 min. at 142° C.

8	
First latex crepe	100.0
Zinc oxide	5.0
Sulfur	3.0
Tetramethylthiuram disulfide	0.4
	108.4

Cure: 20 min. at 127° C.

9	
First latex crepe	100.0
Zinc oxide	5.0
Sulfur	3.0
Mercaptobenzothiazole	0.4
Tetramethylthiuram disulfide	0.2
	108.6

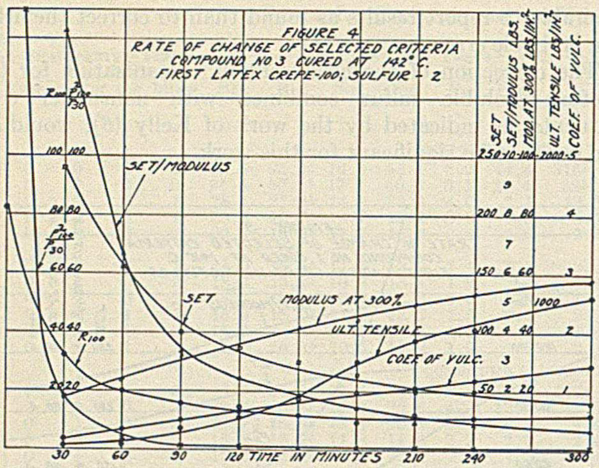
Cure: 20 min. at 127° C.

10	
First latex crepe	100.0
Zinc oxide	5.0
Sulfur	3.0
Diorthotolylguanidine	0.6
	108.6

Cure: 90 min. at 143° C.

Discussion of Results

Measurement of Vulcanization. While it would be convenient to have a single quantitative test which could



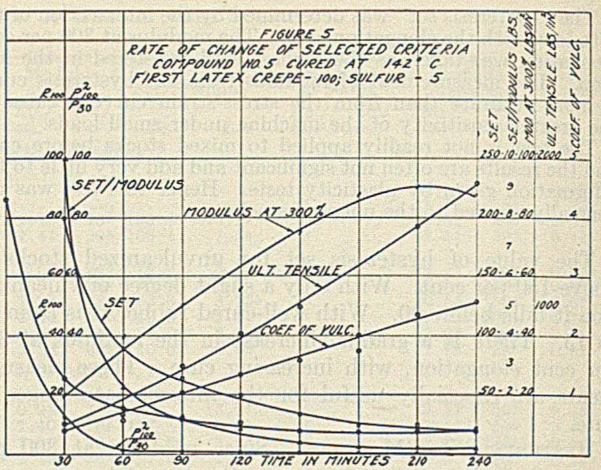
be applied to all types of compound as a measure of the degree of vulcanization, no such test has been found which would be acceptable, even within the limits of compounding and processing used for this study. The milling test is the closest approach, and it is not sufficiently sensitive for quantitative use. A group of tests is therefore necessary. The use of the complete set of tests described above gives a good composite picture of the degree of vulcanization. In some cases the changes measured follow so closely the same trend that only one measurement need be used. The tests with greater sensitivity and higher precision are more dependable than the others. A comparison of the results obtained with many stocks indicates that a satisfactory set of criteria for high-gum stocks mixed according to AMERICAN CHEMICAL SOCIETY procedure can be based on measurements of plasticity (Goodrich plastometer), hysteresis, and stress-strain. Table III gives a summary of the selected criteria together with approximate limiting values for unvulcanized and vulcanized rubber.

TABLE III. SELECTED CRITERIA OF VULCANIZATION AND APPROXIMATE LIMITING VALUES

CRITERION	TEST	APPROX. LIMITING VALUES Unvulcanized rubber	Well-vulcanized rubber
R_{100}	Plasticity	60	10
P_{100}/P_{30}	Plasticity	250	1
Set	Hysteresis	150	10
Set/modulus	Hysteresis	10	0.1
Modulus at 300%, kg./cm.²	Hysteresis	1.41	24.6
Modulus at 500%, kg./cm.²	Stress-strain	1.41	70.31
Ultimate tensile, kg./cm.²	Stress-strain	1.41	351.5

The range between these limits is available for measuring the degree of vulcanization. Practically all of the change in the plasticity factors, R_{100} and P^2_{100}/P_{30}, takes place in the earliest stages of the cure. On the other hand, most of the change in tensile strength and modulus takes place in the later stages of cure. While about half of the decrease in hysteresis set and set/modulus takes place early in the cure, the change through the intermediate cures is sufficient to give a useful measure in this range.

CHANGES DURING VULCANIZATION. All of the properties measured change with time of cure. They do not, however, all vary at the same rate. Typical changes are shown in Figures 3 to 5. The relation between the plasticity changes and the tensile changes is particularly interesting. The former are largely complete before the latter become significant. The hysteresis set measurements, depending as they do both on plasticity and tensile characteristics, give values whose variation is intermediate between that of the other two. The great drop in thermoplasticity in the earliest stages of cure is remarkable.



These results suggest the probability that during vulcanization a mechanical structure is built up. Comparatively small structural effects are necessary to exert a large effect on plasticity. The development of tensile, however, requires increasing strengthening of the structure. A rough illustration would be the building of a wooden scaffold. Comparatively few nails are required to hold the structure in shape. For strength, however, it is necessary to drive many nails in many places.

LITERATURE CITED

(1) Bridgwater, E. R., *Rubber Age* (N. Y.), 24, 439 (1929).
(2) Bruni, G., *Rev. gén. caoutchouc*, 8 (75), 19 (1931).
(3) Crawford, R. A., and Bramann, G. M., unpublished work done in this laboratory.
(4) Dieterich, E. O., and Davies, J. M., IND. ENG. CHEM., Anal. Ed., 3, 297 (1931).
(5) Karrer, E., Davies, J. M., and Dieterich, E. O., *Ibid.*, 2, 96 (1930).
(6) Kelly, W. J., J. IND. ENG. CHEM., 12, 875 (1920).
(7) Kindscher, E. (in K. Memmler's Handbuch der Kautschukwissenschaft), p. 296, S. Hirzel, Leipzig, 1930.
(8) Kratz, G. D., Flower, A. H., and Coolidge, C., *India Rubber World*, 61, 356 (1920).
(9) Physical Testing Comm., Rubber Div., Am. Chem. Soc., *Rubber Age* (N. Y.), 26, 429 (1930).
(10) Schidrowitz, P., *India Rubber J.*, 63, 65 (1922).
(11) Shepard, N. A., *Am. Soc. Testing Materials, Symposium on Rubber*, March 9, 1932, p. 30.
(12) Weber, C. O., *Gummi-Ztg.*, 17, 898 (1903); "Chemistry of India Rubber," p. 283, Griffin & Co., London, 1909.
(13) Weber, L. E., *Caoutchouc & gutta-percha*, 13, 8978 (1916).
(14) Wiegand, W. B., IND. ENG. CHEM., 18, 1157 (1926).
(15) Williams, I., *Ibid.*, 16, 362 (1924).

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GERMANY'S CHEMICAL INDUSTRY IN FIRST HALF OF 1933. Although German exports of chemicals and allied products showed a larger decline during the first half of 1933 in comparison with a similar period in 1932 than did those of its two chief competitors, the United States and Great Britain, Germany maintained its position as the world's largest exporter of these products. During this period the I. G. Farbenindustrie added 5000 additional workers to its pay roll, and imports of chemicals, mostly materials for use in the chemical industry, increased 12 per cent in quantity.

Since the low point in the chemical industry's depression in the late summer of 1932, approximately 9000 additional workers have been added to the Farbenindustrie's pay roll. With the further addition this year, it is believed that the I. G. now has around 102,000 employees, as compared with 98,716 at the end of 1931. Part of the increase is due to artificial measures for spreading employment.

Gossypol in the Technology of Cottonseed Oil

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GOSSYPOL is a unique polyhydroxy phenolic compound which apparently occurs only in plants of the cotton family (*Gossypium*). Since cottonseed may contain as much as 0.6 per cent of this reactive substance, some of the irregularities encountered in processing cottonseed oil have a definite relationship to the gossypol content. A majority of the published researches on gossypol have been concerned chiefly with its toxic properties, and the work of Withers and Carruth (*11*), Schwartze and Alsberg (*7*), and others indicate that the toxicity of free gossypol is an important factor in cottonseed injury resulting from the injudicious feeding of cottonseed meal. In the present paper, however, gossypol has been investigated along lines having a direct bearing on problems of cottonseed oil milling and refining.

The complete structure of the gossypol molecule is not known. Clark (*2*) assigns it the molecular formula $C_{30}H_{30}O_8$, and classifies it as a phenolic substance containing six hydroxyl groups, the remaining two oxygen atoms being present as carbonyl groups. Two of the hydroxyl groups are decidedly more acidic than the other four, and, upon titration in aqueous solution, it reacts like a strong dibasic acid. Gossypol is insoluble in water, very slightly soluble in petroleum ether, soluble in alcohol, concentrated sulfuric acid, ether, trichloromethane, and aqueous alkalies, though in the latter medium it darkens and oxidizes rapidly. Its best known derivatives are the acetate, $C_{30}H_{30}O_8 \cdot CH_3COOH$, used in isolating gossypol from the seed extract, and the dianiline derivative, $C_{42}H_{40}N_2O_6$, which, owing to its crystalline character and insolubility, is used for quantitative estimation (*1*). Dianiline gossypol is insoluble in alcohol, petroleum ether, ether, and vegetable oils. It is somewhat soluble in boiling benzene, trichloromethane, and aniline, and may be recrystallized readily from any of these solvents.

Although gossypol is quite stable in many respects when in the pure crystalline state, it appears to undergo transformations in the seed during storage, cooking, and pressing. Cold-pressed or expeller oil generally contains a considerable amount of unchanged gossypol, but application of the usual aniline precipitation methods to hydraulic pressed oil and to the ether extract of cottonseed meal yield only traces or none at all. Clark postulates that gossypol condenses with the amino groups of the seed proteins in a reaction analogous to the formation of dianiline gossypol, and he terms the resulting ether-insoluble complex "bound gossypol." This assumption is supported by the fact that treatment of the meal with hot aniline will extract the majority of bound gossypol as a dianiline gossypol which is very similar to, if not identical with, dianiline gossypol (*3*) prepared from pure gossypol. It has also been noted that mild heating of ether extracts containing gossypol in the presence of atmospheric oxygen induces changes in the molecule which render it nonprecipitable, and a more or less spontaneous oxidation and decomposition occur when alkaline solutions of gossypol are exposed to the air. Therefore when the pyridine-aniline method[1] developed in this laboratory showed, by direct precipitation, the presence of gossypol in crude hydraulic cottonseed oil, it was suspected immediately that problems concerning excess refining losses and poisoning of the saponification catalyst in the acid splitting of soapstock were closely linked with the gossypol content. It is well known that many crudes give a refining loss out of proportion to free fatty acid and nonfat content (Wesson abso-

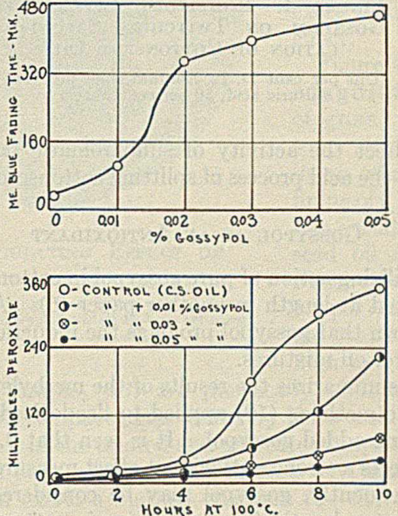

Figure 1. Antioxidant Effect of Gossypol Added to Refined Cottonseed Oil

Above, methylene blue stability test; below, peroxide-accelerated oxidation method

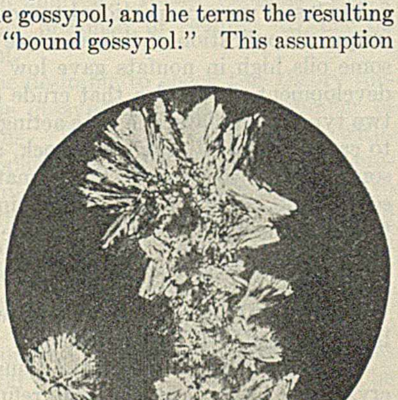

Figure 2. Gossypol Recrystallized from Ether-Alcohol Mixture (× 300)

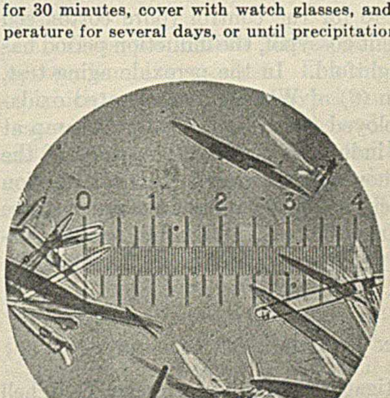

Figure 3. Dianiline Gossypol Recrystallized from Hot Benzene (× 300)

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[1] This method in detail has been made the subject of a separate report. The essentials are as follows: Fifty grams crude cottonseed oil are weighed into a 250-ml. beaker and diluted with about 70 ml. petroleum ether. If a precipitate forms, allow to stand overnight and filter. To the filtered sample add 3 ml. aniline and 12 ml. pyridine. Agitate on a mechanical stirring rack for 30 minutes, cover with watch glasses, and allow to stand at room temperature for several days, or until precipitation has ceased. Filter on tared Gooch crucibles, wash with petroleum ether, dry, and weigh. If the dianiline gossypol crystals are contaminated with amorphous sediment, extract the precipitate with hot benzene, dry, and reweigh. Loss in weight is recorded as di aniline gossypol.

Halverson and Smith's method [Ind. Eng. Chem., Anal. Ed., 5, 29 (1933)] recommending ethylene glycol to be used with aniline for the determination of free gossypol in meal, which appeared after the completion of this work, has been tested tentatively on hot-pressed oil, but it has not proved satisfactory.

lute oil method), owing to a poor break, and neutral oil entrained in the soap stock. It will be shown that gossypol has an important bearing on the type of break obtained in alkali refining, and also that small amounts of gossypol may seriously affect the activity of sulfoaromatic saponification catalysts in the acid process of splitting cottonseed foots.

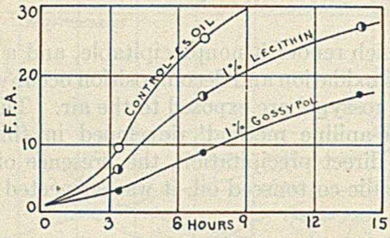

Figure 4. Inhibitory Effect of Gossypol on Twitchell Saponification of Cottonseed Oil

(One per cent D. P. Kontakt, one per cent sulfuric acid, 50 per cent water)

Gossypol as an Antioxidant

The stabilizing action of pure gossypol in cottonseed oil has been reported at length in another paper (*6*). Also Mattill (*5*) has shown that gossypol prolongs the induction period of lard–cod liver oil mixtures.

Figure 1 summarizes the results of the methylene blue and the peroxide methods (*10*) applied to deodorized cottonseed oil containing added gossypol. It is seen that 0.05 per cent gossypol exerts a strong antioxidant effect measured by either test; consequently, gossypol may be considered the most abundant natural antioxidant occurring in cottonseed, which has been identified to date, and that it is this compound which accounts largely for the superior resistance to rancidity of dry, filtered crude over refined cottonseed oil.

The gossypol used in this and subsequent experiments was isolated and purified by Clark's method (*2*). It was obtained as yellow crystals (melting point, 205° C., uncorrected; molecular weight by titration with 0.25 *N* sodium hydroxide, 530). The crystalline form of the free gossypol and of the dianiline derivative is shown in Figures 2 and 3. Therefore it is improbable that any of its properties described in this paper can be due to impurities.

The methylene blue fading times are roughly proportional to the oxidative induction period. For example, a concentration of antioxidant which doubles the fading time will approximately double the induction period. If the fading time is increased from 40 for the control (pure cottonseed oil) to 320 for 0.02 per cent gossypol, the induction period has been increased about eightfold. In the peroxide aging test, the writers' modification (*6*) of Wheeler's accelerated oxidation apparatus was employed, using light (200-watt lamp at 15 cm.) to shorten the induction period. The slope of the peroxide value curve shows the duration of the induction period, and, since a rancid flavor generally develops in these samples at peroxide value of 60 to 80 millimoles, the stabilizing effect of gossypol is readily apparent from the curves in Figure 1.

Gossypol as an Inhibitor of Hydrolysis

Trusler (*8*) has investigated naturally occurring Twitchell catalyst poisons in vegetable oils and uses the term "antihydrol" to designate those substances which inhibit saponification. He found that lecithin retarded hydrolysis markedly and infers that this phospholipid is responsible for the resistance to hydrolysis shown by crude cottonseed oil. Figure 4 shows that gossypol is more effective than lecithin as a saponification inhibitor, under the conditions of this experiment. The oil was agitated with an equal volume of water at 95° to 100° C., to which was added one per cent Kontakt, one per cent sulfuric acid, and one per cent gossypol or vegetable lecithin. Samples were drawn at intervals and analyzed for free fatty acid. Since gossypol is appreciably soluble in warm, moderately concentrated sulfuric acid, it appears probable that the custom of acid-washing acidulated foots prior to splitting concerns the removal of gossypol and gossypol decomposition products as well as destruction of phospholipids. While crude cottonseed oil shows a considerable phosphorus content, only a fraction of this may be calculated to lecithin, and the amount of gossypol in an average crude, as determined by the pyridine-aniline method, may equal, or in some cases exceed, the lecithin content.

Effect of Gossypol on Refining Loss

In order to produce choice edible oil from crude cottonseed oil, it is generally admitted that some sort of alkali refining is necessary. This peculiarity of crude cottonseed, in distinction to many other crude vegetable oils which may respond satisfactorily to less drastic treatment, has been explained by referring to the high resin and nonfat content of the former. Admittedly the terms "gums," "resins," and "nonfats" used in this connection can cover a wide latitude, but their ambiguity renders such an explanation inadequate. In addition, these so-called resins and gums are invoked to account for the abnormal refining losses frequently met with in the commercial refining of crude oils from different mills. Prior to the development of Wesson's method (*9*) for absolute oil determination, the idea was prevalent that the excess refining losses were proportional to nonfat content. However, frequent application of this absolute oil method showed that some oils high in nonfats gave low losses. This led to the development of the idea that crude cottonseed oil contained two types of nonfats, one type acting as an emulsifying agent to cause flocculent, oily soap stock, and the other serving in some manner to promote the formation of compact, oil-free soap stock. While many emulsifying agents have been detected in the nonfat portion of crude oil (*4*), such as lecithin, resins, phytosterol, phytosterolin, nitrogenous products formed by the hydrolysis of seed proteins, and traces of water-soluble gums, the compounds which promote low losses have not been identified completely.

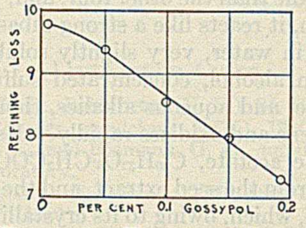

Figure 5. Effect of Added Gossypol on Refining Loss of Crude Hot-Pressed Cottonseed Oil

(Free fatty acid, 1.6 per cent; official A. O. C. S. test refining method)

Figure 5 shows the effect of adding small amounts of pure crystalline gossypol in the alkali refining of an average grade of hydraulic-pressed cottonseed oil (Birmingham mill, free fatty acid, 1.6 per cent; loss by official A. O. C. S. test refining, 9.8 per cent). Without the added gossypol this oil gave the characteristic light colored, spongy, and flocculent foots commonly obtained with a low free fatty acid–high loss oil.

When 0.1 per cent or more of gossypol was dissolved in the alkali just before mixing with the oil, the resulting foots settled out as a dark compact mass, from which the supernatant oil could be drained readily. Soap stock analysis for neutral oil and fat saponified showed that the main reduction in loss was accounted for by low neutral oil, although the fat-saponified loss was also less than that for the control. Apparently the gossypol interacts with the naturally occurring emulsifying agents, rendering them inert. Since it is known that gossypol reacts readily with the amino group (aniline), the suggestion is made that protein fragments (proteoses, peptones, amino acids) are the chief causes of oily soap stock, and that gossypol functions by chemical reaction with these bodies, possibly changing their colloidal structure and solubility. A few high-loss oils have been encountered which do not respond to the gossypol treatment. Usually these oils show an abnormally high acetyl value, indicating the presence of considerable mono- or diglycerides. A mixture of synthetic mono- and diglycerides was prepared from cottonseed fatty acids, and it was found that addition of a small percentage of these to a low-loss crude increased the refining loss several per cent. Furthermore, when the monoglyceride-treated crudes were refined with added gossypol, no appreciable reduction in loss was noted.

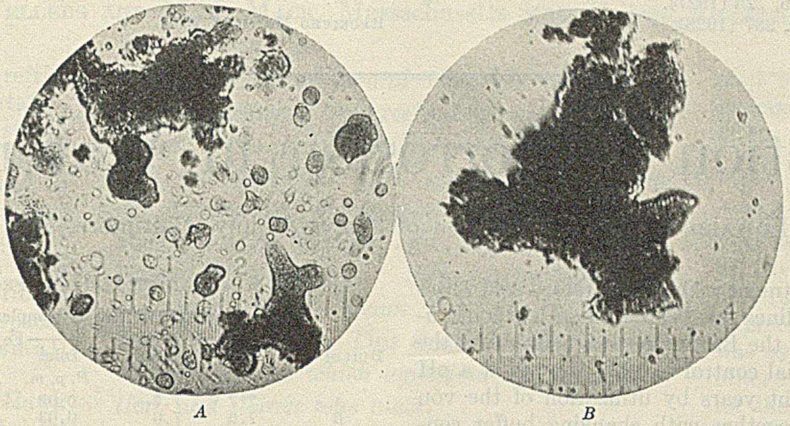

FIGURE 6. PHOTOMICROGRAPHS SHOWING COAGULATING EFFECT OF GOSSYPOL (× 40)

A. Soap stock break on Greenville high-loss cottonseed oil refining (free fatty acid, 1.6 per cent; loss, 11.2 per cent). *B.* Same as *A* with 0.1 per cent gossypol added before refining.

These facts have led to the formulation of a refining theory for cottonseed oil. High (excess) loss oils may be classed in two groups: (1) high in protein bodies, low in gossypol; and (2) low in nonfats (protein, gums, gossypol, etc.), high in mono- or diglycerides. Likewise, low-loss oils may be largely placed in one of two classes: (1) high in gossypol, low or average in protein bodies; and (2) low in nonfats, low in mono- and diglycerides.

This theory explains why excess refining losses cannot be predicted by absolute-oil analysis. It also explains the low neutral oil loss generally obtained in refining expeller oil which is high in gossypol.

Obviously, it would be desirable to check this theory further by determining the gossypol content of a number of high-loss and low-loss oils. This has been attempted, without great success, by application of the pyridine-aniline precipitation method. While this method shows from 0.02 to 0.15 per cent gossypol in many hot-pressed oils which yield none at all with the old aniline method, there is still some form of heat-modified gossypol which resists precipitation even in the presence of pyridine. This has been proved by adding 0.2 per cent gossypol to a crude oil, dividing the sample into six parts, and heating portions to the following temperatures for 30 minutes: 80°, 100°, 120°, 140°, 160°, 180° C. The amounts of gossypol recoverable by precipitation decrease with increasing temperature, and in the 180° sample, no gossypol at all precipitates. Clark (*2*) claims that pure gossypol is heat stable at such temperatures, so that possibly no deep-seated chemical change has taken place, and, while the gossypol is nonprecipitable, it may still function as a refining aid.

Further proof of the gossypol refining theory may be had by considering the adverse effect of iron salts in the refining mixture. Ferrous sulfate (0.2 per cent) added to the lye dose will increase the refining loss on an average oil from 1 to 5 per cent. This is largely a result of the interaction of the iron salt with gossypol, as seen by the characteristic black precipitate which darkens the soap stock. The gossypol in this form cannot function as a refining aid, and the naturally occurring emulsifying agents are free to exert their maximum effect.

Figure 6 shows the coagulating effect of gossypol on the soap stock obtained in an official test refining of a high excess-loss, crude cottonseed oil (Greenville, Miss., free fatty acid, 1.8 per cent; loss 11.0 per cent). The large flocs in the gossypol-treated sample (6*B*) are practically oil-free and settle out as a dark compact mass with very little occluded neutral oil. Analysis of the treated and untreated soap stock showed 4.6 and 15.2 per cent neutral oil, respectively, indicating that the gossypol exerts a marked effect on the character of the foots.

It would be interesting from a theoretical standpoint to have a better understanding of the exact mechanism involved in the flocculation and settling of soap stock in the refining kettle, particularly with respect to the interfacial phenomena involved. Further study along such lines, coupled with a better knowledge of the structure and reactivity of gossypol should also be valuable aids in putting cottonseed oil refining on a more scientific basis.

SUMMARY

1. Gossypol is the chief natural antioxidant in cottonseed. The stabilizing effect of pure crystalline gossypol added to refined cottonseed oil has been measured by means of methylene blue fading time, and peroxide-accelerated oxidation curves.

2. Gossypol inhibits the saponification of cottonseed oil by the Kontakt catalyst. Experimental Twitchell batches to which one per cent gossypol and one per cent lecithin, respectively, were added showed that gossypol retards splitting more effectively than lecithin. This property of gossypol is used to explain the advantages of an acid preboil in the commercial Twitchell treatment of acidulated soap stock.

3. Gossypol plays an important role in the alkali refining of crude, hot-pressed cottonseed oil. The presence of gossypol in most hot-pressed oils can be shown by using the aniline-pyridine precipitation method; and, by moderate heating of oils to which pure gossypol had been added, it is shown that a crude oil may contain up to 0.2 per cent heat-modified gossypol which is nonprecipitable by any known method. Refining losses on certain oils have been lowered 1 to 3 per cent by the addition of fractional percentages of pure gossypol.

A refining theory for hydraulic-pressed cottonseed oils which show abnormal losses is outlined.

ACKNOWLEDGMENT

The authors wish to acknowledge with thanks the helpful suggestions of L. C. Haskell, under whose direction this work was conducted.

LITERATURE CITED

(1) Carruth, *J. Am. Chem. Soc.*, 40, 647 (1918).
(2) Clark, *J. Biol. Chem.*, 75, 725 (1927).
(3) Clark, *Oil & Fat Ind.*, 5, 237 (1928).
(4) Jamieson and Baughman, *Ibid.*, 3, 347 (1926).
(5) Mattill, *J. Biol. Chem.*, 90, 141 (1931).
(6) Royce, in press.
(7) Schwartze and Alsberg, *J. Agr. Research*, 5, 261 (1915).
(8) Trusler, *Oil & Fat Ind.*, 8, 141 (1931).
(9) Wesson, *Ibid.*, 3, 297 (1926).
(10) Wheeler, *Oil & Soap*, 9, 89 (1932).
(11) Withers and Carruth, *J. Agr. Research*, 5, 261 (1915).

RECEIVED March 13, 1933.

Reduction of Corrosion in Water Pipe

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CORRECTIVE treatment with lime to retard cold water corrosion of pipe lines has been more or less continuously practiced in the Baltimore water supply for the past ten years. The initial control in 1922 (*1*) was at a pH value of 8.3, but in recent years by utilization of the von Heyer (*4*) marble test, together with changing buffer conditions, a satisfactory protective coating has been maintained at a pH of 7.9.

To determine if adequate protection is being given, a study of the corrosive properties of the water in two large office buildings was undertaken. Building A is 3.5 years old with no corrosion in the lines, and B is 28 years old with incrusted pipe. Both are about 6 miles distant and on a direct service from the plant. Samples were collected weekly over a period of 11 months. As shown by the analytical data in Table I, the protection is sufficient at a pH value of 7.7. In the older building these results indicate that slight corrosion is occurring with immediate precipitation of the insoluble hydrated oxides by the alkaline water. The practical value of this control is shown in Figure 1. The pipe specimens were obtained from the service supplying these buildings and are comparable to the pipe in them. Pipe 1 was in service about 20 years, the others only 5 years. The protective value of corrective treated waters is apparent.

Contrary to experience elsewhere and as has been previously indicated (*5*), no reduction in pH value has been found anywhere in the system which consists of 1500 miles of pipe lines and two open balancing reservoirs. As shown by weekly samples, collected over a 2-year period from twenty-seven different points on the system, an average pH of 7.8 was maintained in the water leaving the plant, and this value did not decrease at any point in the city. It is believed that, when such reduction does occur, the water was not initially brought to the calcium carbonate equilibrium curve. The example cited by Hechmer (*3*) is characteristic. The initial pH in this supply was about 7.4 with a value of 6.6 at the end of the line. This is below the calcium carbonate saturation point, which in accordance with the Baylis (*1*) curve would be between 8.5 and 9.0. Removal of all aggressive carbon dioxide is impractical, as it would probably produce caustic alkalinity. This inability to remove entirely the carbon dioxide explains the continuance of the corrosion found in these lines. Such conditions stress the necessity of continuous lime application to give pipe protection, controlled either by automatic pH recording devices or frequent testing with color standards. Intermittent application does not produce good coatings.

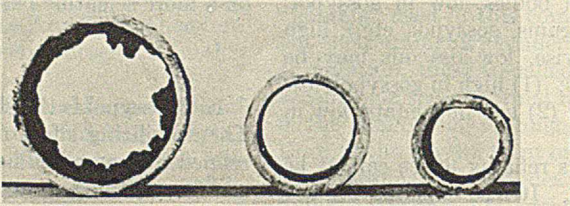

FIGURE 1. TYPICAL PIPE SPECIMENS FROM BALTIMORE WATER SYSTEM

TABLE I. ANALYTICAL DATA FROM OFFICE BUILDINGS

(Average analysis of weekly samples for 11-month period)

BUILDING	pH Inlet	pH Outlet	Fe Inlet	Fe Outlet	O_2 Inlet	O_2 Outlet
			P. p. m.	*P. p. m.*	*Cc. per liter*	
A	7.7	7.7	0.03	0.03	5.5	5.8
B	7.6	7.6	0.03	0.04	5.6	5.2

COST DATA

The cost of lime treatment to maintain a pH value of 7.9 in this water for 1932 was $0.14 per million gallons. It is unwise to attempt an evaluation of the increased years of service given to pipe lines by corrective treatment. There are many variables to be considered; external electrolysis is perhaps the most common. The operating and maintenance costs for pipe lines owned by this bureau for 1932 were $8.41 per mile less than for 1920 when corrective treatment was not used. Conditions other than alkaline water enter into this cost reduction, but its noncorrosiveness is an important factor.

Corrective treatment by lime increased the total hardness of the water about 9 p. p. m. According to Buswell's data (*2*) about 900 pounds of soap per million gallons was necessary to soften the water actually used for laundry and washing purposes. Since it is impossible to determine the quantity of water so used by consumers and also to obtain a correct soap evaluation, an assumption of financial cost would be questionable. Reduction in repair bills, a minimum of property damage caused by corrosion leaks, elimination of staining of clothes and fixtures more than compensate for the added soap cost to the consumer. The total saving to the community is great and does not compare in any degree to the added slight cost entailed by the increased hardness.

LITERATURE CITED

(1) Baylis, J. R., *J. Am. Water Works Assoc.*, 9, 408 (1922).
(2) Buswell, A. M., "Chemistry of Water and Sewage Treatment," p. 80, Chemical Catalog, 1928.
(3) Hechmer, C. A., *J. Am. Water Works Assoc.*, 19, 369 (1928).
(4) Heyer, von, Tillmans, and Heublein, "Die Untersuchung und Beurteilung des Wassers und Abwassers," 4th ed., p. 40, Ohlmuller u. Spitta, 1915.
(5) Hopkins, E. S., "Water Purification Control," p. 105, Williams & Wilkins, 1932.

RECEIVED March 2, 1933. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 85th Meeting of the American Chemical Society, Washington, D. C., March 26 to 31, 1933.

Vitamin C Content of Strawberries and Strawberry Ice Cream

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Howard Supreme and Klondike varieties of fresh strawberries are excellent sources of vitamin C, only two grams giving good weight gains and full protection from scurvy. Preservation of strawberries by freezing, with or without sugar, has no harmful effect on the vitamin C content of the fruit. Strawberries when incorporated in ice cream show no measurable loss of vitamin C. This is attributed to the low temperatures at which agitation, air incorporation, and storage take place.

WITH modern refrigerated transportation methods, fresh strawberries are found in the public markets from December to August. Strawberries have thus become increasingly important from a dietary viewpoint. The fruit is also extensively frozen both with sugar (frozen-pack) and unsweetened. A small quantity is also canned.

Smith, Bergheim, and Hawk (*4*) presented no data but briefly reported that scorbutic guinea pigs were cured in seven days by the daily administration of 10 cc. of freshly expressed strawberry juice. Juice which had been boiled for 5 minutes was equally active in curing scurvy. Kohman, Eddy, and Halliday (*1*) determined the protective dose of strawberries (variety unnamed) to be 2 to 3 grams. Autopsy findings were not reported. They found Oregon canned strawberries to be of about the same potency. Scheunert (*2*) in Germany assayed several varieties of fresh strawberries and found the daily protective dose to be 5 grams or less. Canning and preserving slightly decreased the vitamin C potency.

No data have been reported on frozen strawberries, in spite of the fact that this is by far the most important method of preservation. Frozen strawberries are now available the year round in many stores. Furthermore, huge quantities are frozen-packed with sugar for use in the preserve, sirup, bakery, and ice cream industries. Early in 1932 a study of fresh and frozen strawberries and strawberry ice cream was begun to ascertain the effect of manufacturing processes on the vitamin C content of the fruit.

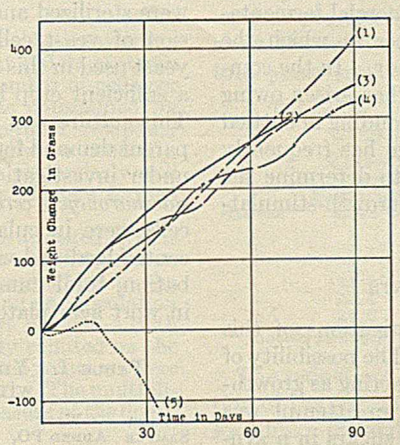

Figure 1. Vitamin C in Fresh and Frozen Strawberries and Strawberry Ice Cream

(1) Frozen strawberries, no added sugar, 2 grams; scurvy score, 0.
(2) Fresh strawberries, 2 grams; scurvy score, 0.
(3) Frozen-pack strawberries with sugar, 2:1, 3 grams, equivalent to 2 grams of unsweetened fruit; scurvy score, 0.
(4) Strawberry ice cream containing 30 per cent of frozen-pack strawberries (*3*), 10 grams equivalent to 2 grams of unsweetened fruit; scurvy score, 0.
(5) Negative control.

Experimental Procedure

The Sherman, La Mer, and Campbell method (*3*) was used with the exception that the amounts fed were proportioned to the weight of the guinea pigs—i. e., a 400-gram animal was fed four-thirds as much as one weighing 300 grams. The animals were all young and healthy, weighed between 280 and 325 grams, and were housed in individual cages. The basal ration consisted of 58 per cent equal parts of rolled oats and wheat bran, 30 per cent of milk powder free of vitamin C (baked), 10 per cent butter fat, 1 per cent each of cod liver oil and salt. Water was kept before the animals at all times.

Three guinea pigs normally were used at each feeding level. At the end of the feeding period all animals were chloroformed and carefully examined for lesions of scurvy. Negative controls died in 26 to 33 days with an average Sherman scurvy score of 14.

Samples

Two lots of fresh strawberries were fed: (1) mainly Klondike variety shipped from the South, and (2) locally grown Howard Supreme. The Klondike variety was available for only 50 days; other mixed varieties were used for the last 22 days. Similarly, Howard Supreme was fed for 46 days, and mixed ever-bearing varieties for the last 26 days of the experiment.

Howard Supreme variety, frozen with sugar in the ratio of two to one and held in freezing storage at 0° F. (−17.8° C.) was fed in the first test. The berries were packed into one-gallon cans. Small samples were removed from the cans as needed, thawed, and fed to the animals.

In the second test, unsweetened Klondike strawberries, frozen and stored by the Birdseye Laboratories in one-pound waxed paper cartons, were used. These berries had been in storage from 4 to 7 months.

The ice cream mix consisted of 12 per cent vitamin C–free butter fat, 10 per cent baked skim milk powder, 15 per cent sugar, 0.30 per cent gelatin, and 63 per cent water, and it was pasteurized at 150° F. (65.6° C.) for 30 minutes, homogenized at 3000 pounds per square inch (211 kg. per sq. cm.) pressure, cooled to 40° F. (4.4° C.), and aged for 20 hours at 40° F.

Thirty per cent of defrosted, frozen-packed Klondike strawberries (two parts of fruit to one of sugar) was added to the mix at the beginning of the freezing process. The freezing process required 10 minutes, after which the ice cream was drawn from the freezer into cans at an overrun of 90 per cent and a temperature of 23° F. (−5° C.). The ice cream was held at −5° F. (−20.6° C.) until used (1 to 3 months). Ten grams of ice cream thus contained the equivalent of 2 grams of strawberries.

Results

The results are given in Table I and Figure 1 and clearly show that both fresh or frozen Howard Supreme and Klondike strawberries are richly endowed with vitamin C. Two grams daily, the lowest quantity fed, were fully protective from scurvy and produced large weight gains. There was apparently no loss in the freezing and storing processes either with or without sugar. Similarly, when frozen-packed strawberries were used in strawberry ice cream, they retained their

Table I. Vitamin C Assay of Fresh and Frozen Strawberries and Strawberry Ice Cream

Product	Animals	Daily Dosage	Av. Gain in Weight	Av. Survival Period	Scurvy Score	Remarks
		Grams	*Grams*	*Days*		
Fresh, Howard Supreme strawberries	3	2	300	70	0	Berries available only 70 days
	3	4	287	70	0	
Fresh Klondike strawberries	3	2	337	72	0	Berries available only 72 days
	3	4	299	72	0	
Frozen strawberries with sugar; 2 parts berries to 1 of sugar	2	3	345	90	0	....
	2	6	269	90	0	
	2	9	− 12	90	0	
Strawberry ice cream, containing 30% frozen-pack berries as above	4	10	320	90	0	One animal died at end of 41 days; no scurvy
	4	15	222	90	0	One animal died at end of 26 days; no scurvy
Frozen strawberries; no added sugar	3	2	425	90	0	One animal sick during last 2 weeks of period; no scurvy
	3	3	285	90	0	
	3	4	270	90	0	
Negative control	2	0	−102	33	13	Severe scurvy

original antiscorbutic potency. In spite of the beating in of air and agitation by the dasher of the freezer, the low temperature must exert a marked protective action on the vitamin C. In this laboratory similar treatment at higher temperatures with tomatoes and cranberries has caused marked losses of vitamin C.

Attention is called to the depressing effect on growth of excessively large doses of either strawberries or strawberry ice cream. This effect has been repeatedly noted in other vitamin C assays and may be due to the disturbing effect on the digestive and nervous systems and to the unbalancing of the diet. In spite of poor or even negative weight gains, no scurvy was found on autopsy in any animal in this experiment.

Acknowledgment

The Klondike frozen strawberries were packed, frozen, and stored by the Birdseye Laboratories, Gloucester, Mass.

Literature Cited

(1) Kohman, E. F., Eddy, W. H., and Halliday, N., Ind. Eng. Chem., 20, 202–4 (1928).

(2) Scheunert, A., "Der Vitamingehalt der deutschen Nahrungsmittel. I. Obst und Gemüse," Springer, 1929.

(3) Sherman, H. C., La Mer, V. K., and Campbell, H. L., *J. Am. Chem. Soc.*, 44, 165–72 (1922).

(4) Smith, C. A., Bergheim, O., and Hawk, P. B., *Proc. Soc. Exptl. Biol. Med.*, 19, 228 (1921).

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Yeast-Growth Stimulants in White Sugars

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The presence of stimulating substances in sugar and other materials is highly important in fundamental studies of yeast metabolism, in commercial fermentation processes, and in many other instances in which the growth of such microörganisms is a vital factor. In the commercial manufacture of beverages difficulty has arisen owing to the development of yeast precipitates or clouding in bottled goods during storage. This type of spoilage has frequently been attributed to sugars, and an attempt to determine the extent and probable importance of nonsugar growth-stimulating substances has been made.

Salts as Possible Stimulants

Most synthetic media selected for investigations of this nature contain sucrose as a basic nutrient. The possibility of salts (carried in the sugars as contaminants) acting as growth-promoting substances was considered, and an attempt was made to detect their presence by using the sugars in a synthetic medium which had been deprived of one or another of its necessary ions. In the early part of this investigation each sugar was added to Fulmer, Nelson, and Sherwood's medium F (*2*) from which first one and then another of the recommended salts had been eliminated.

This medium F contains ammonium chloride, calcium chloride, dipotassium phosphate, calcium carbonate (precipitated), dextrin, and sucrose. The first test was to determine whether the phosphorus was adequate. Medium F was prepared in 100-cc. quantities with and without added phosphates, and the different sugars were added. (Potassium was provided in the form of potassium carbonate.) The media were sterilized and inoculated with 0.1 cc. of a water suspension of yeast cells from a 24-hour wort agar slant. (The yeast used in this study was isolated from a beverage in which a sufficient crop had developed to cause a visible sediment. This culture was well suited to this study because of its apparent demand for the particular growth-promoting substance under investigation. It has been identified as a variety of *Saccharomyces cerevisiae*.) From three to ten thousand yeast cells were inoculated into each flask. The cells had been centrifuged and washed repeatedly. After 48 hours of incubation, total numbers of viable organisms were determined in wort agar plates. The results are shown in Table I.

Table I. Yeast Growths Obtained in Medium F with and without Phosphates

Sugar Sample	With Added PO_4	Without Added PO_4	Sugar Sample	With Added PO_4	Without Added PO_4
1	4,820,000	2,640,000	4	7,000,000	33,000
2	2,120,000	900,000	5	476,000	7,000
3	7,840,000	630,000	6	544,000	3,000

It is evident that the addition of phosphates to the modified medium (i. e., medium F complete) increased the growth with every sugar tested. This indicated that, in general, the sugars were not supplying sufficient amounts of this salt, although the amount of growth in sample 1 indicated that that particular sugar furnished sufficient phosphates for marked yeast development.

With no added phosphates, some growth took place, varying with different sugars. While at first this might indicate that the sugars were supplying definite quantities of phosphates to the medium, it must be borne in mind that in a medium in which no phosphates were present some yeast development might be expected on the first subculture from a medium as rich in nutrients as wort agar. In general, however, it can be concluded that these sugars did not carry sufficient phosphates to be significant.

In a similar manner the same sugars were tested for their ability to provide the nitrogen necessary for growth. These results are shown in Table II.

TABLE II. YEAST GROWTHS OBTAINED IN MEDIUM F WITH AND WITHOUT NITROGEN

SUGAR SAMPLE	WITH ADDED N	WITHOUT ADDED N	SUGAR SAMPLE	WITH ADDED N	WITHOUT ADDED N
1	7,840,000	4,500,000	4	476,000	220,000
2	4,820,000	2,460,000	5	544,000	15,000
3	2,120,000	540,000	6	7,000,000	13,000

These results indicate that some of the sugars contained ample nitrogen to support abundant yeast growth and others did not, suggesting that the stimulants were nitrogen compounds. However, these sugars were also under study in the Carbohydrate Division of this bureau, where exhaustive chemical analyses were being made. By a comparison between the analytical data available there and the results of the fermentation tests, it appeared that there was no direct correlation between the amounts of nitrogen present and the stimulating abilities of the sugars.

ABILITY OF SUGARS TO SUPPORT YEAST GROWTH

It was observed, however, that the yeast used in this study grew in sterilized, 10 per cent solutions of many of the sugars without the addition of nutrient salts. As this solution offered a ready means of studying the abilities of different sugars to support yeast growth, it was used in place of medium F in the remainder of this investigation. The solutions were made up in 100-cc. quantities and sterilized in 300-cc. Erlenmeyer flasks at 15 pounds for 20 minutes. With this new medium, slight modifications in inoculations and cell counting were adopted:

> All flasks were seeded with an inoculum prepared by transferring a portion of a 24-hour wort agar growth to about 100 cc. of sterile distilled water. After vigorous shaking the number of cells per cubic centimeter of the water suspension was determined by direct microscopical counting, with a double-ruled Neubauer hemacytometer (eight hundred squares were always counted). (The yeast used in the above experiments was particularly well suited to counting by this method, since any clusters formed were readily broken up by shaking.)
>
> The strength of the inoculum usually was then adjusted so that each cubic centimeter contained between three and five million cells. One cubic centimeter of this inoculum was added to the 100 cc. of sugar solution in each flask, producing an inoculation which led to moderate growth if nutrients were present. Both the inoculum and subsequent crops were readily counted on the Neubauer slide without dilution. The inoculated solutions were incubated at 30° C. for 72 hours and then counted. The multiplication of yeast cells was used as an arbitrary measure of the quantity of nutrients present.

A series of sugars was tested in 10 per cent solutions by the technic described above. Some did not support yeast growth, while others produced comparatively large yeast crops. Results typical of this part of the investigation are given in Table III, in which the sugars are arranged in the order of ascending yeast counts. For convenience the number of cells per cubic centimeter of the original sugar solution immediately after inoculation is recorded as one unit, and the total crop after growth as a multiple of this number.

TABLE III. MULTIPLICATION OF YEAST CELLS IN 10 PER CENT SUGAR SOLUTIONS

SAMPLE	MULTIPLE OF COUNT AFTER INOCULATION	SAMPLE	MULTIPLE OF COUNT AFTER INOCULATION
A	1[a]	H	16
B	1	I	21.7
C	3	J	34
D	4	K	36
E	6	L	58.5
F	8	Inoculum	1
G	13		

[a] 1 indicates no increase in numbers.

One hundred seventeen samples of white sugars have been studied in this way, the samples being collected during a period of three years. Marked differences in ability to support yeast growth were evident, both between sugars collected in the same year and between those collected in different years. Larger yeast crops than those recorded in Table III have been noted, especially during the earlier part of this investigation. The lesser stimulation in the more recent samples may be due to improvement in quality, or to changes in the growth and metabolism of the yeasts after they have been maintained on laboratory media for some time.

STUDY OF STIMULANTS

Since it was found that some sugars did not support growth, while others produced excessive crops, attention was directed to a study of the stimulants. Several sugars, some of which promoted yeast growth and some not, were extracted with alcohol in a manner similar to that described by Devereux and Tanner (*1*), which was designed for the removal of yeast growth-promoting substances from plant materials. The sugars were dissolved in hot distilled water until saturated solutions resulted. After the solutions had cooled, the saturated sirups were removed, and to them sufficient 95 per cent ethyl alcohol was added to result in an alcoholic concentration of 80 per cent. The sugar crystallized out from these solutions. The crystallization was usually complete within 96 hours. The alcoholic liquor was then removed from the crystallized sugar by decantation and reserved for future studies. The sugar was dried, powdered, and bottled as alcohol-purified sucrose.

The growth-promoting abilities of the alcohol-purified sugars were then compared with those of the unpurified sugars in 10 per cent solutions. The same method of testing was used as previously outlined. The results given in Table IV show the influence of alcohol purification in reducing the total yeast crops.

TABLE IV. YEAST CROPS OBTAINED WITH SUGARS USED BEFORE AND AFTER PURIFICATION

	MULTIPLE OF YEAST INOCULUM[a]			MULTIPLE OF YEAST INOCULUM[a]	
SAMPLE	Unpurified sugar	Purified sugar	SAMPLE	Unpurified sugar	Purified sugar
1	1	1	7	27.0	9.5
2	1	1	8	31.0	10.0
3	3	1	9	34.5	1.3
4	11.3	6.6	10	44	3.0
5	22.6	3.0	11	59	12.0
6	24.0	9.6	12	87.8	1.0

[a] Inocula strength, 1.

The reductions in yeast crops obtained by alcohol purification of the sugars are similar to those obtained by Funk and Freedman (*3*) and suggest that the growth-promoting factors may be related to the more commonly known growth stimulants from plant materials.

However, since minute quantities of certain salts may show stimulative effects upon cell growth, it appeared advisable to test their influence on yeast development. The ash from a sugar which showed marked growth stimulation was added to 10 per cent solutions of a nonstimulating sugar. Counts on the yeast crops obtained showed that the salts in the ash had exerted no stimulative influence. This, with the information gained previously, led to the conclusion that the stimulating substances contained nitrogen, were organic, and were soluble in 80 per cent alcohol.

Further studies on the relation of the growth-promoting factors to known growth stimulants of plant origin, on the possible importance of carbons, filter aids, etc., as well as the importance of such stimulants to bacteriological fermentation tests, are now under investigation.

Acknowledgment

All of the sugar samples used in this investigation were furnished by the Carbohydrate Division of this bureau. The authors appreciate the advice and assistance given by H. S. Paine, J. A. Ambler, and other members of the Carbohydrate Division.

Literature Cited

(1) Devereux, E. D., and Tanner, F. C., *J. Bact.*, 14, 317–33 (1927).
(2) Fulmer, E. I., Nelson, V. E., and Sherwood, F. F., *J. Am. Chem. Soc.*, 43, 186–91 (1921).
(3) Funk, C., and Freedman, L., *J. Biol. Chem.*, 56, 851–60 (1923).

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Beating Properties of Egg White

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Methods have been devised for studying the increase in volume of egg white on beating, and the stability of the beaten product. The effects of rate and time of beating, temperature, hydrogen-ion concentration, and additions of water and oil have been determined, and also the comparative results obtainable with fresh and defrosted storage white.

In the course of an investigation dealing with the use of beaten egg white in a commercial candy product, it was necessary to determine the effect of various conditions on volume of the beaten white and the relative stability of the foam. There is little information of a quantitative character to be found in the literature and no very satisfactory methods for the measurement of either foam volume or foam stability. St. John and Flor (*6*) used a method which consisted in beating the egg white with a hand beater until an apparent maximum volume was obtained, drying the foam in an oven at 60° C. to a solid condition, breaking it into small pieces, and measuring the volume approximately in a graduated cylinder. They obtained better results with the thin than with the thick white, and better results with storage than with fresh eggs. They also found that contamination of the whites with a trace of yolk has a detrimental effect on the beating qualities, a fact which has long been known in commercial practice.

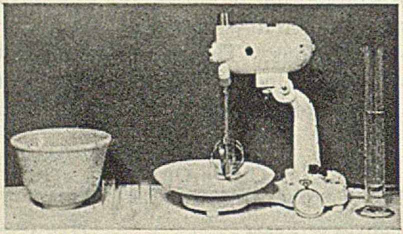

Figure 1. Apparatus

Peter and Bell (*5*), using a penetrometer method, compared the stability of foams made by beating solutions of dried whey protein and of dried egg albumin. In the case of the whey protein they obtained increased stability by small additions of calcium hydroxide and subsequent neutralization; by successive small additions of acid or alkali during whipping; and by the addition of tannic acid, saponin, sodium sulfite, or sodium disulfite. No attempt was made by these workers to measure the beaten volume.

So far as can be learned from their published results, none of the above investigators attempted to determine the most satisfactory time of beating, speed of agitation, or temperature during beating, and to standardize their procedure accordingly.

Methods and Apparatus

It was felt that much more satisfactory results could be obtained with a mechanical beater with speed control, in place of the hand beater used by the preceding workers. The apparatus used in all the following determinations was a Sunbeam Mixmaster kitchen beater, manufactured by the Chicago Flexible Shaft Company. It was provided with a rheostat permitting its use at four different speeds.

The increase in volume on beating the egg white was determined as follows:

Small glass cylinders, open at both ends, of inside dimensions about 17 × 50 mm., were used for the determinations. The volume of these cylinders was carefully measured, and the weight of liquid egg white which they would contain was calculated, assuming the specific gravity of the white to be 1.035.

To determine the volume increase of the egg white after beating, one of these tubes was pushed into the beaten mass until completely filled, care being taken to exclude large air bubbles and to leave no part of the tube unfilled. The excess was removed from the ends of the tube by scraping off with a

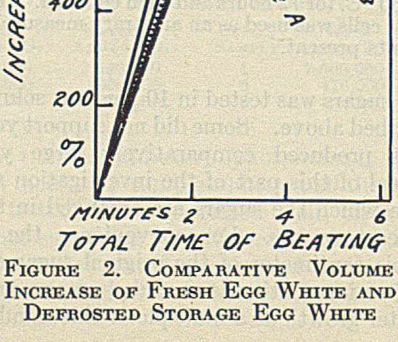

Figure 2. Comparative Volume Increase of Fresh Egg White and Defrosted Storage Egg White

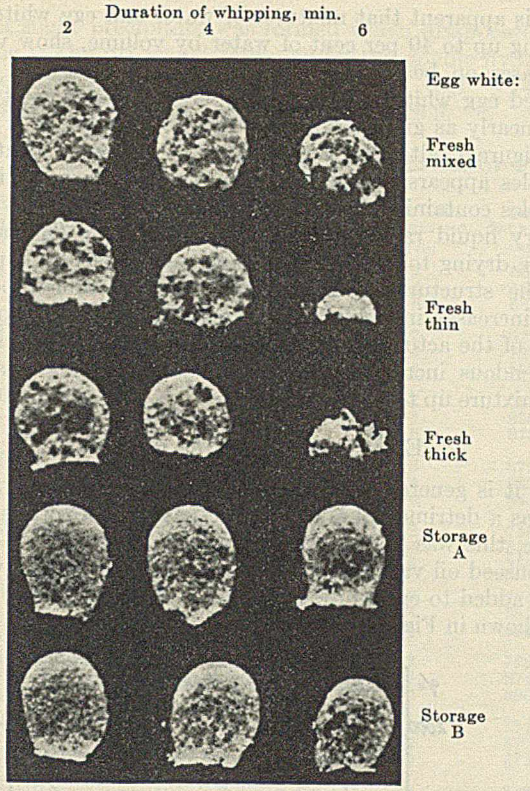

FIGURE 3. COMPARATIVE STABILITY OF FRESH EGG WHITE AND DEFROSTED STORAGE EGG WHITE

sharp-edged spatula, the outside of the tube was carefully wiped dry, and the tube and contents were weighed. Since the increase in volume on beating is proportional to the decrease in weight of a given volume, this increase may be expressed as a percentage of the original volume as follows:

If the tube content $= W$ grams of liquid white
$= w$ grams of beaten white
then the percentage increase in volume is equal to

$$100\,\frac{W}{w} - 100 = 100\left(\frac{W}{w} - 1\right)$$

The relative stability of the beaten white was determined by pushing the sample out of the sampling tube on to a sheet of clean glass by means of a glass rod flattened at the end. The sample was then allowed to dry slowly at room temperature. When dry, the material, which was more or less collapsed in some cases, was sectioned transversely with a razor blade, and the sections photographed to show the structure of the product and the degree to which collapse had taken place. The equipment used is shown in Figure 1. (Unless otherwise stated all determinations were made on frozen storage egg white, after defrosting.)

EFFECT ON VOLUME INCREASE OF BEATING SPEED AND TIME OF BEATING

Seventy-five cubic centimeters of the egg white were placed in the mixing bowl at 20° C. The beaters were started while still raised out of the material: when constant speed was attained, as tested with a tachometer, the beaters were lowered suddenly into the egg white and the stop watch was started. At the end of the first time interval shown, the beaters were stopped and a sample taken. (The sampling required about one minute.) The beaters were again started and the procedure repeated. Time intervals were chosen in proportion to the speed of beating in order to give approximately maximum volume before the end of the longest interval.

The results obtained are shown in Table I. Duplicate runs were made at 1220 r. p. m. in order to determine how closely the results could be checked from time to time. The speed giving the greatest volume increase was thus 1080 r. p. m. and this speed, and the time intervals of 2,4, and 6 minutes were adopted for all further tests.

TABLE I. EFFECT OF SPEED AND TIME OF BEATING ON VOLUME INCREASE

(Temperature 20° C.)

BEATER SPEED	TOTAL TIME OF BEATING	WEIGHT CONTAINED IN SAMPLE TUBE		INCREASE IN VOL., $100\left(\frac{W}{w} - 1\right)$
		Liquid (W)	Beaten (w)	
R. p. m.	*Minutes*	*Grams*	*Grams*	%
580 (Not beaten enough in 10 minutes to permit taking samples)				
710	2.5	12.02	2.19	447
	5.0	11.91	2.11	465
	7.5	12.83	2.18	488
1080	2	12.02	1.76	582
	4	11.91	1.41	741
	6	12.83	1.44	788
1220	1	12.02	1.77	575
	2	11.91	1.66	616
	3	12.83	1.73	641
1220	1	12.02	1.82	561
	2	11.91	1.75	580
	3	12.83	1.81	608

EFFECT OF TEMPERATURE

Seventy-five cubic centimeter samples were adjusted to 10°, 15°, 20°, and 25° C. and beaten as described above. The results at 15°, 20°, and 25° C. were within the experimental error of the method. The results at 10° C. appeared to be somewhat lower. The temperature of 20° C. was adopted for subsequent experiments. A rise of temperature of about 3° C. was found to occur during the beating.

COMPARISON OF FRESH EGG WHITE AND FROZEN (DEFROSTED) STORAGE EGG WHITE

In view of the results reported by St. John and Flor (*6*), the results obtained by the present method on two commercial egg white samples from different sources, which had been frozen and held in storage in this condition for a considerable time, were compared with determinations on perfectly fresh eggs. At the same time, tests were made separately on the thick and thin fractions of the fresh white.

Fresh eggs, graded "extras" by the Canadian Government standard, were broken, and the white carefully separated from the yolk. The further separation into thick and thin white was carried out on a 9-mesh screen by the method of Holst and Almquist (*1*). The proportions of thick and thin white in the various samples are shown in Table II. The results on beating are given in Figure 2.

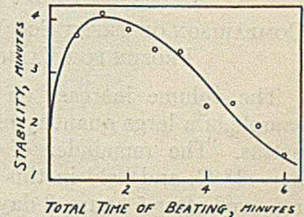

FIGURE 4. EFFECT OF TIME OF BEATING ON STABILITY OF BEATEN FRESH EGG WHITE

TABLE II. PROPORTION OF THICK AND THIN WHITE IN FRESH AND FROZEN (DEFROSTED) STORAGE EGG WHITE

SAMPLE	THICK WHITE	THIN WHITE
	%	%
Fresh extras	58.4	41.6
Frozen storage A	28.0	72.0
Frozen storage B	26.0	74.0

The results indicate that the thin white has considerably better initial beating properties than the thick fraction, but that the former tends to lose volume on continued beating. The properties of the mixed fresh white are intermediate between the two, as would be expected, while the mixed defrosted storage whites give results which are much inferior to the mixed fresh white.

On these samples, stability tests were made by the method already described. The photographed sections of the dried cylinders of beaten white are shown in Figure 3. It is evident that the beaten fresh white is much less stable than the storage white, and that the stability becomes less and less with continued beating.

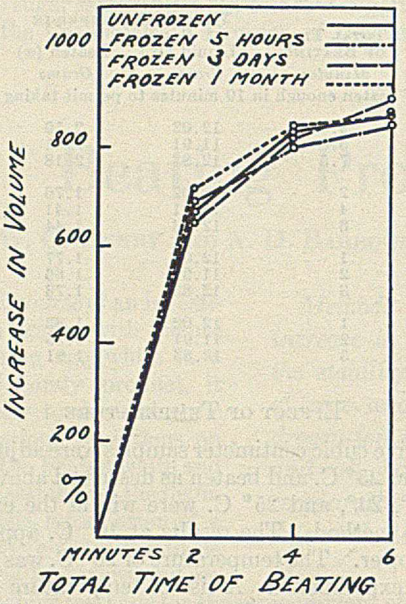

Figure 5. Effect of Freezing and Defrosting on Volume Increase of Fresh Egg White

This effect of beating time on the stability of the beaten fresh white was checked by a penetrometer method similar to that used by Peter and Bell (*5*), with the results shown in Figure 4. These correspond well with the indications of the photographic method.

Comparison of Fresh Egg White and the Same Material Frozen for Various Lengths of Time

The volume increase on beating was determined on a sample of a large quantity of egg white separated from fresh extras. The remainder of the material was frozen solid at −3° C. and held in this condition. Small samples were removed after 5 hours, 3 days, and 1 month, and the volume increase on beating determined at 20° C., after defrosting. The results are shown in Figure 5. It is evident that freezing and frozen storage exerts a negligible effect on the beating properties over the period of the test. The changes in the frozen product which affect the beating quality must accordingly be very slow.

Effect of Additions of Water

It has long been a popular belief among housewives that the addition of a small quantity of water to egg white has the effect of improving its beating properties. It has already been noted that the beaten volume of thin white is greater than that of thick white, although Holst and Almquist (*1*) find that the thick and thin fractions have the same content of total solids.

Mixtures of egg white with water in various proportions, from 98:2 to 20:80, were beaten and the volume increase determined. This has been calculated in two ways: (1) as the increase in volume over the volume of liquid beaten, and (2) as the increase in volume over the actual volume of egg white in the mixture. The results appear in Figures 6 and 7.

It is apparent that mixtures of water and egg white, containing up to 40 per cent of water by volume, show volume increases on beating equal to the volume increase of undiluted egg white. The stability of the beaten mixtures is also nearly as great as for the undiluted white, as is shown by Figure 7, although the structure of the water-containing samples appears, in general, to be more porous. With the samples containing 60 and 80 per cent of water by volume, watery liquid ran out of the beaten samples on standing, before drying took place, and there was a decided tendency for the structure to break down with continued beating. The increases in volume obtained, when calculated on the basis of the actual egg white content of the samples, show a tremendous increase with increasing amounts of water in the mixture up to 80 per cent.

Effect of Additions of Oil

As it is generally supposed that the presence of traces of oil has a detrimental effect on the beating properties of egg white, this was tested experimentally. Amounts of refined cottonseed oil varying from 0.01 to 1.00 per cent by volume were added to egg white samples before beating; the results are shown in Figure 8.

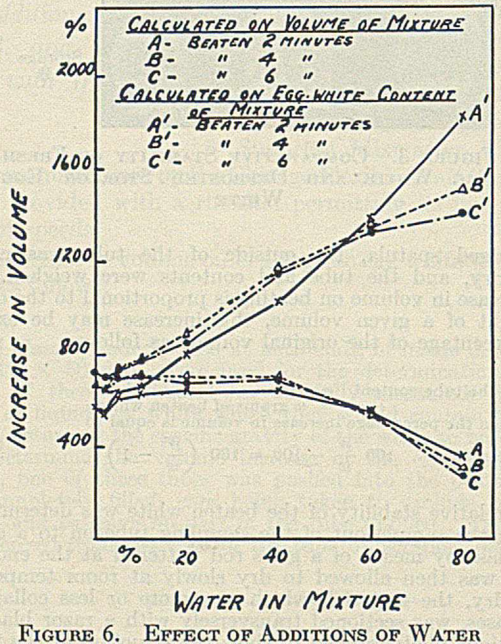

Figure 6. Effect of Additions of Water on Volume Increase

The effect of adding oil to the mixture is to reduce the beaten volume, and the reduction in volume is directly proportional to the percentage of oil added, within the expermental error of the method. The tendency for the structure to break down on continued beating also increases in proportion to the amount of oil added.

The stability of the beaten product is apparently unaffected by additions of oil up to 0.2 per cent. There is a definite breakdown with 0.5 per cent, and with 1 per cent of oil the structure breaks down completely on standing.

Effect of Hydrogen-Ion Concentration

These tests were carried out using fresh egg white, with the normal equilibrium pH of 9.37. The samples were prepared by diluting varying amounts of standard sulfuric acid and sodium hydroxide solutions to exactly 5 cc. and by adding 70 cc. of egg white, 5 cc. of distilled water and 70 cc. of egg white were used as the control. In the case where the largest amount of acid was added (resulting in a pH of

5.47), a slight precipitate was formed which disappeared on standing. The pH was determined by the double hydrogen electrode, using a standard acetate buffer (pH = 4.63). The results are shown in Table III and Figure 9.

TABLE III. EFFECT OF pH ON VOLUME INCREASE OF FRESH EGG WHITE

Acid or Alkali Added		pH	Total Time of Beating	Vol. Increase
	Cc.		Min.	%
5N H_2SO_4	1.50	5.47	2	662
			4	669
			6	688
N H_2SO_4	3.00	7.14	2	623
			4	724
			6	877
N H_2SO_4	2.50	7.66	2	653
			4	836
			6	873
N H_2SO_4	2.00	7.86	2	678
			4	869
			6	844
N H_2SO_4	1.00	8.25	2	748
			4	849
			6	853
N H_2SO_4	0.50	9.08	2	724
			4	862
			6	873
Control	..	9.37	2	728
			4	874
			6	880
N NaOH	0.50	9.56	2	771
			4	877
			6	872
N NaOH	1.00	9.65	2	752
			4	882
			6	837
N NaOH	2.00	10.42	2	812
			4	952
			6	922
N NaOH	5.00	11.06	2	766
			4	936
			6	982

While there are few data in the literature dealing with the viscosity of albumin solutions on the alkaline side of the isoelectric point, the general shape of the curve obtained resembles closely the curves given by Lloyd (*3*) for the swelling of gelatin and collagen in alkaline solution, and for the amount of sodium hydroxide combined with a given amount of gelatin (*2*). The curve resembles also the curves given by Loeb (*4*) for the viscosity of sodium and barium caseinates. It would seem that the volume increase on beating is probably a function of the viscosity, although it would be of interest to compare the present results with direct determinations of both viscosity and surface tension.

The increase in volume tends to become somewhat greater with decreasing hydrogen-ion concentration, this effect becoming much more pronounced above pH 10. The stability results for the samples between pH 8 and 10 are similar to those obtained previously for fresh egg white (Figure 3). The stability of the samples beaten 4 and 6 minutes is greater below pH 8 and above pH 10, with the exception of the sample at pH 5.47, which broke down completely.

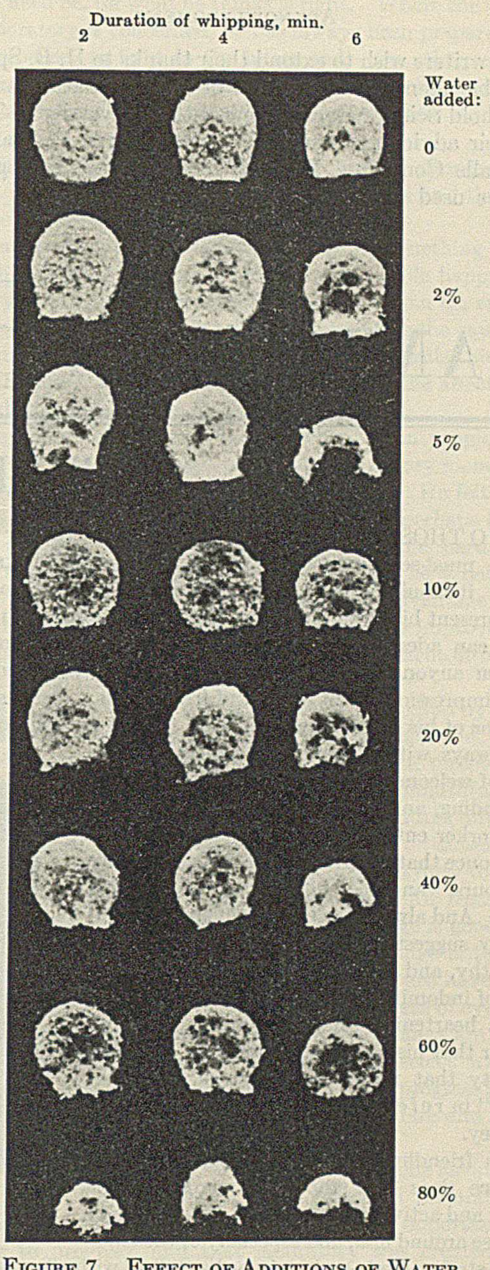

FIGURE 7. EFFECT OF ADDITIONS OF WATER ON STABILITY

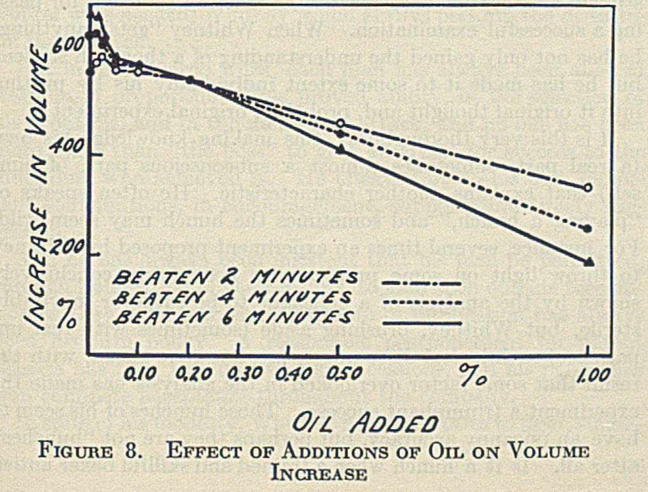

FIGURE 8. EFFECT OF ADDITIONS OF OIL ON VOLUME INCREASE

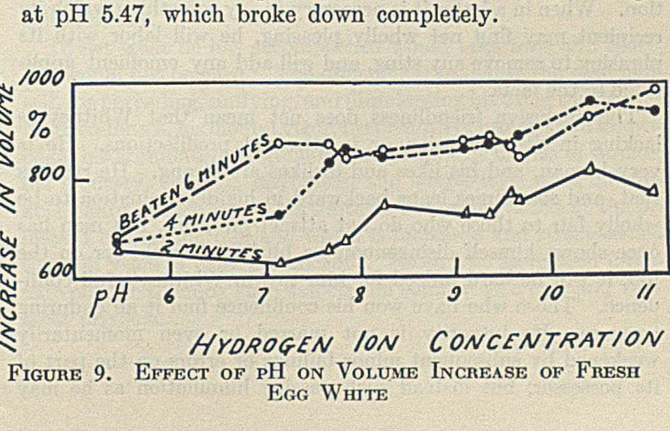

FIGURE 9. EFFECT OF pH ON VOLUME INCREASE OF FRESH EGG WHITE

ACKNOWLEDGMENT

The writers wish to extend their thanks to H. B. Speakman and other members of the staff of the Foundation, and to the Household Science Department of the University of Toronto, for their advice and interest; and to Lorne P. Marshall of Marshalls Company, Limited, for supplying the egg white samples used in this investigation.

LITERATURE CITED

(1) Holst, W. F., and Almquist, H. J., *Hilgardia*, 6, 45 (1931).
(2) Lloyd, D. J., "Chemistry of Proteins," p. 132, J. and A. Churchill, London, 1926.
(3) Lloyd, D. J., *Nature*, 130, 24 (1932).
(4) Loeb, J., "Proteins and the Theory of Colloidal Behavior," p. 87, McGraw-Hill, 1922.
(5) Peter, P. N., and Bell, R. W., IND. ENG. CHEM., 22, 1124 (1930).
(6) St. John, J. C., and Flor, I. H., *Poultry Sci.*, 10, 71 (1931).

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AMERICAN CONTEMPORARIES

Willis Rodney Whitney

TO THOSE who know him, any sketch of Doctor Whitney must seem inadequate. To those who do not know him, it should be said at once that a word picture can no more truly present his dynamic, many-sided personality than a photograph can adequately present a scene of lively, varying action.

When anyone meets Whitney for the first time, one of the initial impressions must be that of friendliness. For many years the door of his office bore the words, "Come in—rain or shine," and always within that door were waiting a smile of welcome, an attentive ear, a quick understanding, and helpful counsel. Any laboratory worker entering that room was made to feel at once that his problem, trouble, or failure was "ours," and that only his success was his alone. And always for each problem he found a ready suggestion, for each trouble a helpful sympathy, and for each failure the encouragement of indomitable optimism, often expressed with a heartening touch of humor. It is no wonder that his associates frequently use in all sincerity that much abused word, "inspirational," in referring to their contacts with Whitney.


WILLIS R. WHITNEY

This friendliness always felt in Whitney's presence does not stop with words. He is keenly and actively interested in the welfare of all those around him, and especially of the laboratory staff. Again and again he has talked with office boys, seeking to learn their interests and aptitudes, suggesting helpful studies, and trying them out on various laboratory jobs in the effort to help them to qualify for better positions. To hurt anyone's feelings unnecessarily is abhorrent to him. More than once when someone has tried with more good will than judgment to do him a personal kindness, Doctor Whitney has taken the trouble to resort to benevolent subterfuge to avoid a seeming lack of appreciation. When in a letter it is necessary to say something which its recipient may find not wholly pleasing, he will labor with its phrasing to remove any sting, and will add any emollient applicable to the facts.

This inclusive friendliness does not mean that Whitney is lacking in discrimination or in personal predilections. He is very human, and his likes and dislikes are strong. He realizes that, and sometimes leans backward in his determination to be wholly fair to those who do not attract him, but, if a man has once shown himself disingenuous, a bluffer, or a slacker on the job, it will be hard indeed for him to win Whitney's full confidence. Those who have won his confidence find it an enduring treasure. Its integrity is not marred or even momentarily weakened by subsequent minor failings or errors on the part of its possessor, but instead such passing humiliation as he may feel is speeded to oblivion by Whitney's prompt manifestation of his unshaken trust.

Two other characteristics which must strike even the casual visitor are his mental alertness and the wide range of his interests and knowledge. His mind is never at rest. Even in his hours of relaxation on his farm he is forever observing, studying, experimenting, and filling in the background by reading. Thus he has developed a series of hobbies which have given him as keen pleasure as golf or bridge can bring to the more sportively inclined. Arrowheads, "doodlebugs," worm galls, and turtles are among those hobbies of his; into each hobby he has put activities of his own, and from each he has derived new facts not in the literature of the subject. He must practice chipping arrowheads himself or try to make artificial worm galls by inserting a bit of steel in a plant stem and warming it by a high frequency field. His hobby may take him into only a little corner of a new field, but that corner he makes his own.

Whitney has said that he was not a facile student when in college, but that he had to work hard for what he got. That statement must seem preposterous to anyone who has discussed any problem with him and has experienced his quick grasp of it, his ready fund of information, his power of rapid analysis, and his promptitude in suggesting lines of attack. It is only through following him into one of his hobbies that the arduousness of his student days is made explicable. Then one begins to see that what Whitney means by "getting" a subject goes far beyond the average student's conception of its mastery, a mastery sufficient for passing a successful examination. When Whitney "gets" anything, he has not only gained the understanding of a thorough student but he has made it to some extent individually his by putting into it original thought and, probably, original experiment.

It is this very thoroughness, this making knowledge his own (a real part, sometimes almost a subconscious part, of himself) that explains another characteristic. He often speaks of "playing a hunch," and sometimes the hunch may seem wild. For instance, several times an experiment proposed by Whitney to throw light on some problem has been fairly conclusively shown by the analysis of a colleague to be futile or inevitably sterile, but Whitney, brushing aside (sometimes with real impatience) such logical discouragement, has gone ahead, with the result that some factor overlooked in the analysis has made the experiment a triumphant success. Those hunches of his seem to have an uncanny accuracy, but perhaps they are not "hunches" after all. Is it a hunch when a trained and skillful boxer anticipates his opponent's blow, seems to "guess" it before it has started, and, like an automatic machine, avoids it and lands a telling blow of his own? Is it not rather long experience instantly reacting through perfectly coördinated eyes and nerves and muscles? And are not Whitney's "hunches" broad experience almost subconsciously reacting through coördinated scientific knowledge, ingenuity, and sound judgment? Certainly all his assistants and fellow-workers have learned to respect those "hunches."

To Whitney the experiment is the thing. Theoretical analysis is good if it points toward an experiment; it is bad if it proves an experiment should not be tried. "Any fool can show me an experiment is useless. I want the man who will try it and get something out of it." His answer to a dogmatically expressed opinion is "Have you tried it?" Long experience has convinced him that in research it is the unforeseeable, or at least the unforeseen, that is forever cropping up. Theorize all you wish, but experiment.

Anything which interferes with experiment is distasteful—red tape, time spent in committee work, and even reports. The report file in his laboratory has been always meager. While he "agrees in principle" that reports are useful, his greater interest in experiment is not conducive to much reporting by his staff. But, as he says, the useful products of the laboratory constitute the best report of its work.

To be forever doing things—investigating, experimenting, "monkeying," as he has called it—is his delight. Like Walt Whitman he may "lean, observing a spear of summer grass," but he could never say with Walt, "I loaf and invite my soul." Activity is his normal state. An old friend of his likes to tell of one summer vacation spent at a lake in western New York when Whitney was a young assistant professor at M. I. T. One day Whitney discovered a shoal in the lake, and immediately it suggested an outlet for his abounding energy. He set to work to build an island on that shoal, bringing tons of rock to build up a huge mound, and surrounding it with a bulkhead to protect it against waves and winter ice. For years "Whitney Island" was the chief point of interest on that lake.

To labor with experimental apparatus is for him, not to work, but to "play with it." When he drops in to see how one of his laboratory staff is progressing in his experiments, a characteristic question is, "Are you having fun today?" Such enthusiasm is contagious, and it is not surprising that Whitney's laboratory has always seemed thoroughly permeated with a true zest for experimental endeavor.

Because of his love of action it is hard for him to delegate minor administrative jobs. It is his natural impulse to do it himself. His assistants have learned by experience that, if a job is delegated, it is well to attend to it on the instant, for otherwise when the assistant gets round to it, he will find that the boss has been there first and the job is done.

One kind of job he has refused, on principle, to delegate—the unpleasant job. If dismissal or admonishment of a laboratory worker were needed, Whitney would always perform the distasteful task himself.

But in his research work, each man has always been allowed freedom in proportion to his proved ability, in the selection of his problems, and in the method of attack, and no one has been more eager than "the boss" to give all credit for success to the individual who achieved it. He always forgets his own important contributions, in encouragement, support, and timely suggestion.

And he has always been insistent that his men be permitted, through publication of their results, to gain such outside recognition as they have merited. Freedom of publication has always been his firm policy. A reasonable postponement for patent reasons has been the limit of his concessions, and his policy has won complete acceptance throughout the company.

In spite of his modesty, Whitney never hesitates to fight, single-handed if need be, for what he thinks is right. Where the welfare of the laboratory is concerned, he has always been prepared, but never compelled, to fight to the bitter end. On other matters, if he is overruled or outvoted, he accepts the decision not only loyally but cheerfully, and proceeds at once to make the best of it.

Compromise, temporizing, indirection are all repugnant to Whitney. He thinks straight through to the end and then sets the shortest course to reach it.

As in all truly lovable characters, there is something of the child in him. He likes fun and likes to see people happy. At laboratory outings no one gets more enjoyment than he, whether in helping the children in their games, in building the camp fire, or in singing around it, and no stranger would recognize him then as "the big boss," except by carefully observing the affectionate respect which meets him on all sides.

Whitney likes simplicity in things as well as in people. His first office in Schenectady was a corner of a laboratory room where one or two men were continually experimenting. He felt doubt about the wisdom of a new laboratory building, perhaps fearing a falling off from plain living, high thinking, and hard work. Even his new office was severely plain. And yet he is not indifferent to comfort. When his associates took advantage of his absence in Europe to refurnish his office and to improve it in convenience, comfort, and appearance, his enjoyment of his new surroundings on his return was evident.

Whitney's philosophy of life has been only indicated by things he has said, but it is implicit in all he does. He has said, "Inactivity and inappreciation in the presence of infinite, undeveloped truth is the most inexcusable type of error and unfaithfulness." The appreciation he demands is active appreciation, intensive search into that "infinite, undeveloped truth." "Research is appreciation." Research thus becomes a duty—a duty to which he has given a lifetime of complete devotion. All research is good, whatever change it may bring, for all change is good in itself. Perhaps we cannot foresee whither all change is tending, but, just as the variations and mutations in nature have made possible, through natural selection, the grand process of evolution and the development of man, so research and change are multiplying the possibilities from which man may select what he needs to help him along the uncertain trail he calls progress toward the far-off, dimly imagined, goal of universal welfare and happiness.

If that philosophy is true, then few men have done as much for ultimate human happiness as he. The Research Laboratory of the General Electric Company has made many important contributions to progress, and that laboratory was created, supported, animated, and inspired by him. But that is not all. His inspirational influence has not been confined within these laboratory walls. His optimism, enthusiasm, sound judgment, and vision have encouraged and stimulated scientists, industrialists, and governmental agencies in widely diverse branches of activity. He has been a catalyzer of far-reaching potency in industrial research. Every man, woman, and child in this country is better off today because Whitney has lived and worked and inspired others.

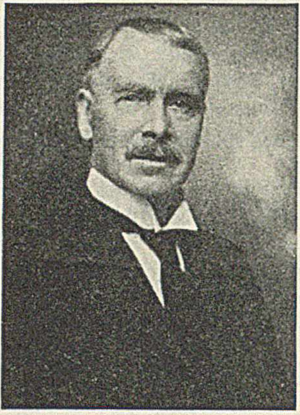
To list what he has accomplished would take time and space, but would not be hard. The difficulty is to depict the man himself, for pervading, unifying, and illuminating his other qualities—his friendliness, his mental vigor, his breadth of interest and knowledge, his stimulating originality, his delightful flashes of humor, his modesty, courage, directness, and simplicity—is an indefinable charm which defies portraiture, but which is felt at the instant of meeting him and which is increased and strengthened through years of close association. Those who have been fortunate enough to enjoy such association count it as a true and very great privilege.

L. A. Hawkins

* * * * *

Peter Spence Gilchrist

THE chemical engineering profession knows him as the Big Little Chief. Small of stature, Peter Spence Gilchrist must be measured by the breadth of his accomplishments. His associates often marvel at the unlimited energy he possesses. In his avid desire for results he will drive his colleagues to exhaustion, while apparently he remains immune to fatigue. His hair is white and his complexion a ruddy pink, an inevitable clue to his English birth. To guess his age, you might suggest fifty-five, or maybe sixty, but never seventy-two! He was born in Manchester, England, in 1861, of Scotch parentage. His father was an engineer, so this son early imbibed the desire also to be an engineer. His desire was an eager one, a relentless one. He was not strong in childhood, but this handicap seemed to strengthen his ability to assimilate his lessons. Manchester educated him, and he arose to the heights that all young engineers of England dream about. He competed for the Queen's Medal and Award, then greatly coveted and only made possible by the dint of severe application and real ingenuity. Queen Victoria presented this medal through the English Government, and it marked a moment that was forever to be an inspiration.


PETER SPENCE GILCHRIST

Like so many Englishmen, he cast his eyes to far horizons, and in 1880 he came to America to install the first mechanical pyrites furnace in this country. He was twenty years old at the time and looked even younger. While he possessed a real confidence in his own ability, there was a lurking fear that on account of his youthful appearance he would not be able to command the respect of his clients. A red mustache was reared for the occasion for dignity's sake, but it failed miserably to allay its owner's extreme youth. Since this lad was installing the furnace that was invented by his father, it was something really personal. This first unit was built in Richmond, Va. Here, he first viewed the South and mentally resolved that some day he would return.

On returning to England, he was retained by Maysworth and Wilson to erect pyrites burners in the company's plants throughout England. While installing one of these units at the North Dean plant, the manager died and Gilchrist was appointed in his place. Here he perfected and put into commercial use the first sulfuric acid plant in the world to produce acid from spent oxide. In 1884 he was made manager of the Peter Spence Alum Works at Goale. Here he met the girl who was later to become his wife. Mr. Gilchrist remained in Goale until 1889. At this period he again turned longing eyes to the west. The memory of that visit to the States now amounted to nostalgia. At home there was a settled position and apparent safety forever. Over the Atlantic lay adventure and promise. That same year he came again to America and was at once appointed in charge of a large fertilizer plant on Long Island.

It was the southern states that he wished to reach, so he declined to remain identified with the New York organization. He opened an office in Baltimore, but later selected Charlotte, N. C., as the potential center of sulfuric manufacture for the southeastern states. His faith in the prospects of this industry and the South were justified. He designed at least fifty plants that produced in excess of 2400 tons of 60° Bé. acid a day. These were mostly built to utilize the pyrites burner of his father. In the course of his intensive service in this field, he forwarded ideas that have now become standard wherever sulfuric acid plants are built. Fertilizer plants naturally fell to his lot, and he designed a large percentage of these. He was one of the pioneers of the phosphate plants in the South, and some of the great phosphate mining plants in Florida were created under his direction. His field was not in the South alone; soon his services were in demand throughout the entire United States and abroad.

In 1914 the Chemical Construction Company was founded by Gilchrist, I. Hechenbleikner, T. C. Oliver, and A. M. Webb, Gilchrist becoming president. The work of this company in heavy acids is well known. While he has had innumerable opportunities to become affiliated with other organizations, he has chosen to concentrate his endeavors in this company.

Simply to give this chronological account of the man's professional career is to leave most unsaid. He has been a pioneer of the boldest type; his constructive ideas have blazed many a path where industries have followed. This long trail is marked with testimonials of its creator. To know Gilchrist, one almost overlooks those professional accomplishments, for they are dwarfed in comparison with the things of life that really matter. Here is a man who has brushed aside the thought of personal gain. He truly lives for others. He has endeared himself to all who know him for his unselfishness. He lives simply content to gain his pleasures among his family. In his work he has made many friends. They respect him and love him, for always he places Christian principles above the desire for gain. His community knows him as a philanthropist who gives without ostentation. When a movement begins that is constructive and good, Gilchrist is often a part of it. A Scotch Presbyterian, he has worked long and untiringly for his church. He has been a ruling elder for almost twenty years; he is on the Board of the Presbyterian Foundation, of the United Welfare Association, and of Queens Chicora College for Women.

Where other men make golf, hunting, or fishing their hobbies, Gilchrist has the Y. M. C. A. He is president of the local Y. M. C. A. and has been on the board of directors for twenty years. His name appears on innumerable committees throughout the South in this work.

A. M. WEBB

Increased Consumption Improves World Synthetic Nitrogen Outlook

The belief that the world synthetic nitrogen industry passed its low point in 1930–31 is supported by the rising trend in world consumption of synthetic nitrogen, which for the first time in some years showed an increase in 1931–32 to a total of 1,421,580 metric tons (N), compared with 1,377,005 in the preceding year, but still notably below 1,586,904 tons in 1929–30. Definite figures are not yet available for the 1932–33 fertilizer year, but it is evident that synthetic consumption is recording a still further increase above 1931–32 levels. In Germany, principal world consumer, indications are that consumption for the current year will record a gain of from 5 to 10 per cent above the 325,000 tons (N) for 1931–32.

The changed trend in world consumption is encouraging in that it marks the termination of a downward trend in progress for several years and represents a better adjustment of output to consumption. On the other hand, the existing excess of production facilities continues to weigh heavily upon the world industry, contributing to increasing unit production costs and exerting a steady pressure on countries for measures to further their own national industries.

CORRESPONDENCE

Pipe Line Protection

SIR: The article "Pipe Line Protection" by Stanley Gill [IND. ENG. CHEM., 25, 49 (1933)] invades a field in which several commercial interests are engaged in competitive relationship and it thus has become difficult for Gill to preserve the neutrality from which he undoubtedly did not desire to depart. Nevertheless, certain portions of the article in question may well be reviewed in the light of more recent data as well as from the point of view of variant commercial practices.

The article was presented by the author at the New Orleans Meeting of the AMERICAN CHEMICAL SOCIETY at the end of March, 1932, or substantially 10 months before its publication in INDUSTRIAL AND ENGINEERING CHEMISTRY. In the meantime there had been further reports in course of development by the American Petroleum Institute (*4*) and the American Gas Association (*2*), as outcomes of the test programs being carried on, respectively, by Scott and Ewing in conjunction with the U. S. Bureau of Standards. These latter reports are not definitely referred to by Gill; they became available to the general reader as references only shortly after the article was published.

It is stated by Gill that "by properly selecting asphalt and wrapper and by exercising care in application, coatings of good protective value can be obtained. Certain petroleum asphalts are entirely unsuitable for pipe-line protection * * * others have been found to be exceedingly stable * * * Asphalts should never be used without the protection of a wrapper."

Concerning coal-tar enamels Gill states, "Coal-tar enamel coatings will afford protection, under some conditions without the use of wrappers." He further states, "The wrapped enamel coatings, which probably possess greater protective value than any currently available coatings of comparable cost, fall into two classes (bonded and unbonded wrap) * * * both, when the work is properly performed, will give coatings of high protective value."

The entire implication therefore is that much more careful selection and application of asphaltic coatings are necessary than in the case of coal-tar enamel coatings, and the asphaltic treatment is definitely singled out as requiring a reënforcing wrapper. The preference for coal tar implied and expressed in Gill's article is not justified by the reports of the American Petroleum Institute associate at the Bureau of Standards. The American Petroleum Institute program of tests involved the burying in 1930 of pipe sections forming parts of actual pipe lines covered with nineteen types of treatments. Nine of the treatments were of coal-tar pitch origin; nine were asphaltic; one was a grease type. Some were thick and some were thin. Some were reënforced with shields or wrappers and some were unreënforced. One, an asphaltic emulsion, was protected with sand-cement mortar; one was an asphaltic mastic. Two, including the one above mentioned, were asphaltic emulsions.

It is presumed that each manufacturer of the coatings in this test sought to present his treatment in the most favorable light; that is, each treatment was the best of its kind at the time. Any improvements in any one since 1930 would be paralleled by presumed improvements in all others.

The over-all results shown in the 1931 (*3*) and 1932 examinations of the test sections were indicative of a low order of protection on the part of coal-tar treatments which had no wrappers. Of the ten treatments which in 1931 and 1932 showed a rating of 80 per cent or higher in effectiveness in prevention of pitting, only three were of coal-tar origin. The rest of the ten in the high effectiveness rating were asphaltic with the exception of one treatment in 1932 which belonged to neither class. In both 1931 and 1932,[1] of the nine rating below 80 per cent in effectiveness, six were of coal-tar origin.

On the basis of cost per ton (an item mentioned by Gill in the above quoted excerpt) asphalts have an advantage over coal-tar enamels. On the basis of thickness of treatment, asphalts have a further advantage as, weight for weight, asphalts will give a thicker treatment than coal-tar enamels.

Gill's article gives equal credit to loosely and closely bonded wraps of reënforcing material over the covering. Yet the one unbonded wrap (asbestos paper) in the A. P. I. tests dropped in effectiveness rating from 0.97 in 1931 to 0.73[1] in 1932. Bonded and melted-in wraps with but one exception (again an asbestos wrap) retained their effectiveness ratings of the year before.

The article by Gill favors asbestos papers in comparison with reënforcing materials of organic origin. But of the three asbestos treatments in the A. P. I. tests, two have a rating of 0.73[1] and 0.62[1] in effectiveness against pitting in 1932 (after having had ratings above 0.90 in 1931). Of the seven treatments having reenforcement of organic origin, all rated above 0.80[1] in 1932.

The American Gas Association's program of tests on underground-pipe protective coatings has paralleled the American Petroleum Institute tests in so far as duration of tests is concerned. However, the American Gas Association tests include no coatings applied to lines in actual service. Conclusions drawn from the tests of the American Gas Association cannot be compared on an equivalent basis to those of the American Petroleum Institute obtained under conditions which bring about certain "long line effects." A comparison indicates that there may be as much as a 1 to 3 difference in the severity of exposure of a coating on a short length of pipe as compared to exposure on a long line, soil conditions being equivalent.

All manufacturers of protective treatments did not submit specimens in the A. P. I. test program. The manufacturer who had probably the longest history with reference to such treatments refrained from entering the test.

The writer of this letter has been connected with corrosion protection work on underground pipe since 1905. It is probable that more severely corrosive soil conditions are met in California than in any other part of the United States. Extensive applications of mechanically applied wraps to pipe, largely by a portable type of machine (*5*) as distinct from isolated local practices of the sort with mill-wrapped pipe, has a decidedly longer history in California than elsewhere.

A noteworthy example of such a treatment is the 16-inch gas transmission line laid in 1929 northward from Buttonwillow, Calif., in the soil generally regarded as the most corrosive in the United States. An example of a similar protection is in the Lindsay-Strathmore and Terra Bella Irrigation Districts where 200 miles of riveted steel pipe ranging from 36 to 4 inches in diameter and from 12 to 16 gage in thickness were laid in 1916–17 in highly corrosive soil [some of this with a corrosion index (*1*) as high as 9 by the nipple and can method]. Not one foot of this pipe has ever been removed because of external corrosion. An example of this type of protection on the Atlantic Coast, employing the same asphaltic materials, is the 31 miles of 75-inch pipe in the Wanaque system of the North Jersey District Water Supply Commission, laid in 1928. Other installations embrace thousands of miles of gas, water, and oil trunk, distribution, and service lines. All of this work has been successfully carried out with asphaltic wrapping materials and asphaltic cementing

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[1] Effectiveness ratings in 1932 are not given in the report but may be calculated from the reported data.

compounds. In the outstandingly corrosive soil of the Pacific Coast there has been used for pipe protection only a negligible amount of the enamels made from coal-tar pitch.

Literature Cited

(1) Corfield, *Western Gas*, 6, No. 3, 25–27 (1930).

(2) Ewing, Scott, Am. Gas Assoc., Distribution Subcommittee Rept. on Specimens Removed in 1932 (1933).

(3) Scott, G. N., Am. Petroleum Inst., *Development Production Eng. Bull.* 208 (1931).

(4) Scott, G. N., *Ibid.*, 210 (1932).

(5) Speller, "Corrosion, Causes and Prevention," p. 532, McGraw-Hill, 1926.

Dozier Finley

The Paraffine Companies, Inc.
San Francisco, Calif.
April 10, 1933

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Sir: I have read Finley's comments with a great deal of interest, and can only say that none of the points which he raises serves to invalidate any of the extremely general conclusions which were stated in my paper. Before the paper was finally handed to you for publication, I was in possession of the data on the second year's inspection of the American Petroleum Institute specimens, and also of the latest data on the American Gas Association tests. I considered these carefully in relation to my paper, and found them to be strictly in line with the statements which I had previously made. It is an unfortunate feature of tests such as those being conducted by Scott for the American Petroleum Institute that test data can be readily misinterpreted as a result of failure to consider all of the factors involved. A detailed refutation of Finley's interpretation of these data would require a great deal of space, and would necessarily enter into technical detail of little or no general interest. I can only reaffirm the conclusions which have been quoted by Finley in his discussion, both as regards the relative merits of coal-tar and asphalt coatings, and of organic wrapping materials, as compared to asbestos felts. It is an unquestioned fact that The Paraffine Companies, Inc., with which Finley is associated, are entirely competent to exercise the care in selection and skill in application which are necessary to obtain good asphaltic coatings; but I do not see that this fact alters in any regard my considered statement concerning the general merits of the various classes of coating materials. As Finley implies in his discussion, it is inevitable that a neutral observer should occasionally offend some of the "several commercial interests * * * engaged in competitive relationship" in the pipe-line coating field, and I can only express my regret that the interests with which Finley is connected should have been among the group which I offended.

Stanley Gill

Rusk Building
Houston, Tex.
April 19, 1933

BOOK REVIEWS

LATEX AND ITS INDUSTRIAL APPLICATIONS. *By Frederick Marchionna.* 1037 + xxiii pages. Rubber Age Publishing Company, 250 W. 57th St., New York, 1933. Price, $15.00.

This volume comprises an extensive and thorough survey of the patent and technical literature on rubber latex. Both patents and literature references are excellently abstracted. Although the author makes no claim for completeness beyond July, 1929, pointing out that from that date the patent literature is either well briefed or fully reported, or translated in *Rubber Chemistry and Technology*, much of the patent literature has been covered up to and through 1932.

The scope of the book is even broader than the title implies. In the 11 chapters there is much information which is not strictly confined to latex. The chapters on rubber plants, planting, and the cultivation of rubber not only contain references to *Hevea brasiliensis*, from which practically all the latex of commerce is derived, but also to guayule, which is not ordinarily considered a latex-bearing plant. In the chapter on methods of preserving latex and rubber, nearly as much attention is given to the preservation of coagulated rubber as to the preservation of latex. A chapter on the behavior and characteristics of latex follows, with specific chapters on the coagulation and preparation of crude rubber from latex. The main section of the book is concerned with the direct application of latex for the manufacture of rubber products. This section comprises nearly half the book and is the most valuable portion, since it brings together in one place the patent literature, well-abstracted, on the various industrial applications.

Each section is introduced with a brief summary on the subject matter of that chapter. These were all written by the author, with one exception. The value of these brief introductory chapters would have been much enhanced had they been written by specialists in the various fields, as in the latter case, and had literature references been given more consistently in discussing the work of the various investigators. Certain inaccuracies have crept into these introductory chapters, obviously as a result of the lack of specific knowledge or experience of the author. For example, acetic acid is given as the most common coagulant of latex. Formic acid had largely supplanted acetic acid for this purpose considerably before 1929. Again, the "superiority of Para rubber" (to what and from what standpoint is not stated) is ascribed to "the degree of the heat of the smoke, which is between 70° and 80° C." This statement is ambiguous and the explanation is questionable.

The style of the author and the clarity of his writing deserves especially favorable comment. The sentences are clear and concise, and the paragraphing is well done. The result is a book which is pleasant to read, in spite of the fact that it is really a reference volume. The method of classification is less commendable. This, coupled with poor choice of type for the headings and poor spacing for these headings, makes consultation of this book for reference purposes annoying in some respects. The author has chosen to classify the patents under each heading under the country in which the patents were granted. This of course results in discontinuity. For example, instead of the United States, British, German, and French patents, issued on the same invention, being grouped together, they are far removed from each other. A further unfortunate procedure was the failure to place the abbreviation of the country before each patent number. The result is that the reader may find it necessary to thumb through many pages to find out to what country the patent number refers. Failure on the part of the publisher to use heavy type and sufficient spacing for the headings makes it difficult to find the subdivisions of the patents. A serious error was made when the names of the assignees of the patents were left out. Omission of the initials of the patentee is also disconcerting, especially where there are several investigators with the same surname.

The subdivisions of the material in Chapter VIII, which covers the direct use of latex in industry, could have been much improved had the 8 parts been further subdivided. The material is listed under such broad headings that one must cover many pages in looking up patent abstracts in any particular field. The placing of the abstracts is not always accurate. For example, in the section on adhesive and coating materials, "latex paints" are interspersed with "seal for containers," "surgical dressings," "aircraft coverings," and "treatment of leather." A subdivision on the compounding of latex would have been especially acceptable.

The adoption of a unique and original set of abbreviations for use in referring to the journal literature seems unnecessary, in view of the fact that most rubber technologists who are interested in latex are thoroughly familiar with the accepted abbreviations of the American Chemical Society. The book has more than an excusable number of typographical errors.

In spite of these criticisms, the author has done a highly commendable piece of work, especially in the manner in which he has abstracted the individual patents. The abstracts are not too brief. They are sufficiently detailed to give the reader a clear idea of what is covered in the patent without reference to the original. This, in itself, is a great service and one which will make the book a valuable addition to any technical library on rubber. N. A. Shepard and H. W. Greenup

LEAD—THE MINERAL INDUSTRY OF THE BRITISH EMPIRE AND FOREIGN COUNTRIES. *By the Imperial Institute.* Second edition, 253 pages. H. M. Stationery Office, London, 1933. Price, paper, 4 s.

The first 44 pages are devoted in general to the mode of occurrence; the ore minerals; the properties of lead; concentration methods; metallurgy; the uses of lead; alloys, shot, solders, brasses, and bronzes; pigments; world production of lead ore (in terms of metal) 1921–32; world smelter production of lead (1921–32); London prices of pig lead for 1908–13 and 1921–32; and a table showing the principal lead mines, smelters, and refiners in the British Empire.

Some 180 pages are devoted to the occurrence, ore minerals, and geology of the lead ore deposits of the British Empire and practically all foreign countries. The metal content of ores and smelter production; the names, location, owners, principal lead and associated mineral deposits; and the tons of ore removed and ore reserves are given for a great number of the countries. Tables show the imports and exports of lead ore, pig lead, finished lead products, etc., for the main producing countries, usually for 1921–32. Tonnages of concentrates and metallic lead produced in 1928–31 are given for most of the countries.

Twenty-six pages are devoted to references to recent technical literature, covering general, concentration, metallurgy, uses, alloys, pigments, and lead in the British Empire and foreign countries.

This book, while of not much practical value to the metallurgist or mining man, should be of value to any one interested in lead and its associated metals. Mining and metallurgical methods in the various countries, except in a few cases, are not given. The volume is up to date and the best of its kind that has come to the reviewer's attention. W. T. Isbell

PURIFICATION OF WASTE WATERS FROM BEET SUGAR FACTORIES. *By E. Hannaford Richards and D. Ward Cutler.* Water Pollution Research Technical Paper No. 3. 157 pages. H. M. Stationery Office, London, 1933. Price, 7 s. 6 d.

Only during the past ten years has the beet sugar industry developed on an extensive scale in Great Britain. With financial assistance from the government the amount manufactured has increased from about 140,000 cwt. in 1922–23 to nearly 10,000,000 cwt. in 1930–31. Since the processes employed in beet sugar factories involve the use of large quantities of water (approximately 3,500,000 gallons per thousand tons of beets extracted), there results serious pollution in the streams into which the waste waters discharge. The Department of Scientific and Industrial Research of the Water Pollution Research Board, in coöperation with a committee from the beet sugar factories, has made studies of the disposal of the wastes. Preliminary experiments at Rothamsted led to the conclusion that biological oxidation on percolating filters was preferable to fermentation with periodic additions of lime or with bio-aëration, or to the activated sludge process. Some of the waste water could be easily purified and re-used. The diffusion and pulp press water were the most important.

Semiplant-scale experiments were then conducted at one of the beet sugar factories at Colwick. It was demonstrated that this process would give a purification of 90 per cent when treated by the process of biological oxidation on percolating filters. The depth of these filters should be about 6 feet, the waste water should be sedimented and diluted so that it will not contain more than 0.1 per cent sucrose. The dilute waste water can be filtered at a rate not exceeding 100 or 150 gallons per cubic yard of filtering material. The most suitable medium for the filters is a hard material such as gravel, flint, or flag. Material should be graded to a size of about $^3/_8$ to 1 inch and should be free from dust.

A thorough study of the organisms present in the filter was made. These include bacteria, fungi, algae, protozoa, rotifers, nematodes, insect larvae, and oligochaetes. Different strains of bacteria were also isolated.

No mention is made of the use of the Steffens process which is important in disposal of wastes from factories in the United States. The references to work on the purification of beet sugar wastes on the Continent and in the United States seem inadequate. Edward Bartow

TWENTY-FIVE YEARS OF CHEMICAL ENGINEERING PROGRESS. Edited by *S. D. Kirkpatrick.* 373 pages. Published by the American Institute of Chemical Engineers, D. Van Nostrand Company, Inc., 250 Fourth Ave., New York, 1933. Price, $4.00, postage extra.

The familiar texts on industrial chemistry are here brought up to date, and this new volume should serve as an inspiring supplement to such familiar treatises. The development and achievements of chemical industries from the viewpoint of thirty-one contemporary chemical engineers are recorded, and interesting side lights on the personalities and agencies contributing to the phenomenal developments in chemical engineering are given.

As its editor points out, this is not a carefully balanced and coördinated textbook, but rather an authoritative array of essays, each interesting in itself and contributing something to the extremely broad picture of the whole development of chemical engineering, particularly in American industry.

One is impressed with the fact that our principal contribution to the industrial machine has been, and is, in producing bigger and better elephants with a minimum of white ones. This may possibly be attributed to a distinctive nationalistic, individual, and industrial courage, the absence of tradition, and the American genius for systematizing and mechanizing. In the field of petroleum and solvent chemistry we may also justly be proud of our fundamental chemical achievements.

In a few of the chapters, particularly those of a historical character, the chemical engineer in assuming the role of author has laid aside his chemical and engineering tools. Adherence to accepted chemical nomenclature, the employment of chemical equations, and the introduction of curves and tables would have done much to make certain essays more instructive. It is surprising that no photographic illustrations were employed, to present more vividly the tremendous strides in chemical engineering development. Incorporation of these details would have made the volume more valuable to large numbers in the chemical fraternity who have not had the benefit of membership in, and excursions with, the American Institute of Chemical Engineers.

All chemists will obtain educational and inspirational benefit from a perusal of this series of essays. It should serve as excellent supplementary reading for courses in the history of chemistry and industrial chemistry. P. H. Groggins

TECHNOLOGY OF CELLULOSE ETHERS. Volumes I to V. *By E. C. Worden, I.* 3396 pages. Published by Worden Laboratory and Library, Millburn, N. J.; exclusive sales agents, Chemical Catalog Company, Inc., 332 W. 42nd St., New York, 1933. Price, $45.00.

It is fortunate that this relatively new field of carbohydrate chemistry and technology should be treated by such an experienced correlator as Worden. The treatment of the subject is along the same lines as that followed by the author in his earlier work with the cellulose esters, there being little attempt to pass on the validity of the literature statements but rather to report faithfully the essentials of the patents and articles abstracted. About 13,173 separate patents and 2800 literary contributions have been edited. Together with the original reference to each piece of work, all abstracts appearing in any important technical periodical throughout the world are listed. The fifth volume is devoted entirely to indexing of patents, names, and subjects which makes it possible to find complete information on any desired subject quickly.

The subject matter has been divided into 15 chapters covering portions of the work which can logically be grouped together; each chapter is further subdivided into topics which bring together all the pertinent facts on a given subject.

A great merit of these volumes lies in the ease with which a particular piece of information may be found. The style and subject matter are not such as to make fluent reading, but as a source of complete information clearly set forth on this class of carbohydrates, this work will be invaluable. D. R. Wiggam

ENGINEER'S MANUAL OF ENGLISH. *By W. O. Sypherd and Charon Brown.* 526 pages. Scott, Foresman and Company, 623 S. Wabash Ave., Chicago, 1933. Price, $2.00.

THIS manual is a workman-like guide to the art of technical writing in its many forms—correspondence, reports, articles, booklets, and specifications.

The authors have concentrated their efforts on the appropriate fashioning and structure of engineering writing and, with the aid of practical examples, have supplied the necessary illumination. Emphasis is laid on arrangement, grammatical completeness, accuracy, and conciseness. It is regrettable that the influence of the subject has resulted in a too short discussion of the great merits of conciseness in all forms of technical writing. Certainly, technical journals provide examples of sentences, paragraphs, and articles which could be pared down with a mutual gain to the writer and the reader.

This is a useful addition to the practicing engineer's shelf of reference works, and it also has merit as an English composition text for engineering students. A. E. MARSHALL

BERL-LUNGE CHEMISCH-TECHNISCHE UNTERSUCHUNGSMETHODEN. Edited by *Ernst Berl.* 8th edition. Volume IV, 1123 pages. Julius Springer, Berlin, 1933. Price, 84 marks.

THE materials dealt with in the present volume are among the most interesting substances which enter the analyst's laboratory. Pages 1 to 200 deal with coke-oven gases, combustible gases in general, and the carbonaceous materials from which they are produced. The impurities—ammonia, gas tar, naphthalene, benzene, the oils for naphthalene absorption and for benzene absorption—are determined as to amount present or degree of saturation by satisfactory procedures. The cyanide compounds cover pages 200 to 238. Coal tar is divided into raw coal tar, the intermediate products, and the finished products. Tar from brown coal has seven divisions, the last dealing with montan wax. The analyses for fats and waxes are divided into selected methods for systematic analysis of fats and technical methods dealing more directly with the products of the several industries. Mineral oils and related substances are treated exhaustively. Essential oils include the essential oils proper and odoriferous materials of any origin. The book concludes with 30 pages on writing and copying inks.

Short methods which will save the analyst's time are numerous. Throughout there are various reproductions of photographs, line drawings, graphs, and tables. There are many cross references, references to the standard periodicals, and to less well-known monographs. The language is clear, direct, and free from involved sentences. The book is highly creditable to its authors for completeness and manner of presentation, and no less so to the printer for the set-up. This volume will be of superior value to the American analyst. E. RAYMOND RIEGEL

SICHERHEITGLAS (VERBUNDGLAS, PANZERGLAS, HARTGLAS, KUNSTDRAHTGLAS). *By H. G. Bodenbender.* 320 pages, 78 illustrations. Chemisch-technischer Verlag Dr. Bodenbender, Feuerbachstrasse 6, Berlin-Steglitz, 1933. Price, 18 marks.

THE author has made an attempt to cover in relatively few pages material which would require volumes to treat adequately. Therefore, all discussions are limited, with the result that the text is little more than an outline; as such it should be of value.

Numerous literature references are given, including the author's concept of the most important patents and a directory of the manufacturers of various types of safety glass.

In a very general way the principles underlying the manufacture of the various types of safety glass, including laminated glass and single-layer safety glass, are discussed. The types of plastic used in multiple-layer safety glass (laminated safety glass) are complete and include the cellulose ester plastics, synthetic resins, gelatin, and the like. The various types of single-layer safety glass include hardened glass, glass reënforced with wire, plastic reënforced with wire, and transparent organic masses usually referred to as synthetic glass or glass substitutes.

The various types of mechanical equipment used in European plant operation for safety glass manufacture are illustrated; diagrammatic sketches for plant layout, personnel requirements, and cost of operation for definite safety glass schedules are given. The mechanical equipment, methods of processing, and bonding adhesives, as described, are at least 3 years behind the American practice for the manufacture of laminated safety glass.

Chapter F which discusses the properties of the various types of safety glass, and Chapter H listing the possible uses for the different types of safety glass, would be of value in aiding one to select a suitable glass for a specific installation. However, the results reported in this book of comparative tests conducted on laminated safety glass made with different cellulose ester plastics, are not representative of American safety glass made with the corresponding plastic. GEORGE B. WATKINS

DAS CELLULOID UND SEINE ERSATZSTOFFE. *By Gustav Bonwitt.* XX + 813 pages, 264 illustrations. Union Deutsche Verlagsgesellschaft, Zweigniederlassung, Berlin, S. W. 19, 1933. Price, 87 marks.

PART I is devoted to a consideration of the raw materials for the manufacture of celluloid and includes a detailed discussion of the process of nitration as well as of the raw materials cellulose, camphor, alcohol, and coloring materials. Part II takes up the manufacture of the celluloid from nitrocellulose and camphor; in addition to the usual manufacturing technic there are included such subjects as alcohol recovery and the chemical and physical tests to which celluloid may be subjected.

Part III discusses in considerable detail the conversion of celluloid into a wide range of products such as combs, hair ornaments, dolls, toys, toilet articles, cane and umbrella handles, and laminated glass. In this classification nitrocellulose lacquers and artificial leather are included. In Part IV there are grouped together the sections devoted to cellulose acetate, cellulose ethers, and plastic masses from casein and the several types of synthetic resins.

To anyone interested in the manufacture and use of the various synthetic plastic materials, particularly those derived from cellulose, this should be a valuable reference book. It is unusual to find so much helpful information collected in a single volume. Furthermore the book is well illustrated and there are frequent references to the original literature.

GUSTAVUS J. ESSELEN

ABSTRACTS OF GERMAN PATENTS (In several volumes). ABSTRACTS OF FRENCH PATENTS. The Patent Abstracting Co., 52 Vanderbilt Ave., New York, 1933. (See the following for prices.)

THE German Patent Office publishes an official journal in which abstracts (*Auszüge*) of the patents are given. These abstracts are about the type of those appearing in *Chemical Abstracts* and are, in general, good. The French Patent Office has a similar system. These books are mimeographed verbatim translations of German *Auszüge* and French Patent Office digests, as follows:

GERMAN PATENT ABSTRACTS:	
Organic Chemistry:	
One volume containing patents issued in 1931	$5.00
One volume containing patents issued in 1932	5.00
Semi-monthly advance copies of patents published in 1933	5.00
Dyes, Varnishes, Lacquers, Paints, Inks, Adhesives:	
One volume containing patents issued in 1931	4.50
Semi-monthly advance copies of patents published in 1933	4.50
Synthetic Plastic Materials:	
One volume containing patents issued from 1897 to June, 1932	4.00
Semi-monthly advance copies of patents published from June, 1932, to end of 1933	4.00
Rubber and Gutta-Percha:	
One volume containing patents issued in 1931, 1932	2.00
Semi-monthly advance copies of patents published in 1933	2.00
FRENCH PATENT ABSTRACTS:	
Chemical Products and Apparatus:	
One volume containing patents issued in 1932	5.00
Semi-monthly advance copies of patents published in 1933	5.00

The books are good and useful. They form convenient references, putting in one place information which is scattered over many pages of *Chemical Abstracts.* The 35-year compilation of German patents on organic plastics is particularly convenient. This period is the most interesting one in the development of the modern synthetic plastics of the synthetic resin type. While not all the important inventions in synthetic resins were made in Germany, the German contribution to the art is substantial.

It is purposed to continue this type of publication and make a permanent service. K. P. MCELROY

MARKET REPORT—AUGUST, 1933

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, AUGUST 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

NEWER CHEMICALS

Acetaldehyde, drums, lc-l., wks.	lb.	.18½
Acetaldol, 50-gal. drums	lb.	.27
Acetylene tetrachloride, *see* Tetrachloroethane		
Acid, abietic	lb.	.06
Adipic	lb.	.72
Furoic, tech., drums	lb.	.35
Linoleic	lb.	.16
Sebacic, tech.	lb.	.58
Ammonium linoleate, drums	lb.	.11
Ammonium oleate	lb.	.10
Aroclors	lb.	.40
Butyl carbitol, *see* Diethylene glycol monobutyl ether		
Cellosolve, *see* Ethylene glycol monobutyl ether		
Furoate, tech., 50-gal. drums	lb.	.60
Calcium furoate, tech., drums	lb.	.30
Capryl alcohol, tech.	lb.	.85
Pure	lb.	2.50
Carbitol, *see* Diethylene glycol monoethyl ether		
Cellosolve, *see* Ethylene glycol monoethyl ether		
Acetate, *see* Ethylene glycol monoethyl ether acetate		
Crotonaldehyde, 50-gal. drums	lb.	.32
Dichloroethyl ether, 50-gal. drums	lb.	.16
Diethylene glycol, drums	lb.	.14
Monobutyl ether, drums	lb.	.26
Monoethyl ether, drums	lb.	.15
Diethylene oxide, 50-gal. drums	lb.	.26
Dimethylamine, pure 25 & 40% sol.—100% basis, drums	lb.	1.20
Dioxan, *see* Diethylene oxide		
Diphenyl	lb.	.20
Ethyl acetoacetate, 110-gal. drums	lb.	.37
Ethyl furoate, 1-lb. tins	lb.	1.00
Carbonate, 90%, 50-gal. drums	gal.	1.85
Chlorocarbonate, carboys	lb.	.30
Ether, absolute, 50-gal. drums	lb.	.50
Furoate, 1-lb. tins	lb.	5.00
Ethylene chlorhydrin, 40%, 10-gal. cbys	lb.	.75
Dichloride, 50-gal. drums	lb.	.05
Glycol, 50-gal. drums	lb.	.25
Monobutyl ether, drums, wks.	lb.	.20
Monoethyl ether, drums, wks.	lb.	.15
Monoethyl ether acetate, drums, wks.	lb.	.16½
Monomethyl ether, drums	lb.	.21
Oxide, cyl.	lb.	.75
Furfuramide (tech.), 100-lb. drums	lb.	.30
Furfuryl acetate, 1-lb. tins	lb.	5.00
Alcohol, tech., 500-lb. drums	lb.	.40
Glyceryl phthallate	lb.	.26
Glycol stearate	lb.	.18
Isopropyl ether, drums	lb.	.07
Lead dithiofuroate, 100-lb. drums	lb.	1.00
Magnesium peroxide, 100-lb. cs.	lb.	1.15
Methyl acetate, 82%, drums	lb.	.12
99%	lb.	.15
Cellosolve, *see* Ethylene glycol monomethyl ether		
Methyl hexyl ketone, pure	lb.	1.20
Paraldehyde, 110–55 gal. drums	lb.	.20½
Phosphorus oxychloride, 175 cyl.	lb.	.20
Potassium abietate	lb.	.06
Sodium abietate	lb.	.03
Sodium alginate	lb.	.50
Strontium peroxide, 100-lb. drums	lb.	1.25
Sulfuryl chloride, 600-lb. drums, crude	lb.	.15
Distilled	lb.	.40
Tetrachloroethane, 50-gal. drums	lb.	.08½
Trichloroethylene, 50-gal. drums	lb.	.09½
Triethanolamine, 50-gal. drums	lb.	.35
Trihydroxyethylamine linoleate	lb.	.40
Trihydroxyethylamine stearate	lb.	.35
Vinyl chloride, 16-lb. cyl.	lb.	1.00
Zinc dithiofuroate, 100-lb. drums	lb.	1.00
Perborate, 100-lb. drums	lb.	1.25
Peroxide, 100-lb. drums	lb.	1.25

CHEMICALS PREVIOUSLY QUOTED

Acetanilide, U. S. P., powd., bbls.	lb.	.26
Acetic anhydride, 92–95%, cbys.	lb.	.21
Acetone, drums, wks.	lb.	.09½
Acetphenetidin, bbls.	lb.	1.25
Acid, acetic, 28%, c/l., bbls.	100 lbs.	2.91
56%, c/l., bbls.	100 lbs.	5.50
Glacial, c/l., bbls.	100 lbs.	10.02
Glacial, U. S. P., c/l., carboys	100 lbs.	10.52
Acetylsalicylic, bbls.	lb.	.70
Anthranilic, 99–100%, drums	lb.	.85
Benzoic, tech., bbls.	lb.	.40
Boric, bbls.	lb.	.04
Butyric, 100% basis, cbys.	lb.	.80
Chloroacetic, mono-, bbls., wks.	lb.	.18
Di-, cbys.	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.04½
Chromic, 99%, drums	lb.	.12
Cinnamic, bottles	lb.	3.25
Citric, U. S. P., cryst., bbls.	lb.	.29
Cresylic, pale, drums	gal.	.45
Formic, 90%, cbys., N. Y.	lb.	.11
Gallic, U. S. P., bbls.	lb.	.74
Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.40
H, bbls., wks.	lb.	.65
Hydriodic, 10%, U. S. P., 5-lb. bot.	lb.	.67
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.35
Hydrofluoric, 30%, bbls., wks.	lb.	.07
60%, bbls., wks.	lb.	.15
Hydrofluosilic, 35%, bbls., wks.	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis	lb.	.75
Lactic, 22%, dark, bbls.	lb.	.04
48%, light, bbls., wks.	lb.	.11
Mixed, tanks, wks.	N unit	.07
	S unit	.08
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls.	lb.	nom.
Nitric, c. p., cbys.	lb.	.11
Nitric, 36°, c/l., cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks.	lb.	.11
Phosphoric, 50%, U. S. P.	lb.	.14
Picramic, bbls.	lb.	.65
Picric, bbls., c/l.	lb.	.30
Pyrogallic	lb.	1.45
Salicylic, tech., bbls.	lb.	.33
Stearic, d. p., bbls., c/l.	lb.	.09½
Sulfanilic, 250-lb. bbls.	lb.	.15
Sulfuric, 66°, c/l., cbys., wks.	100 lbs.	1.60
66°, tanks, wks.	ton	15.00
60°, tanks, wks.	ton	10.50
Oleum, 20%, tanks, wks.	ton	18.50
40%, tanks, wks.	ton	42.00
Sulfurous, U. S. P., 6%, cbys.	lb.	.05
Tannic, tech., bbls.	lb.	.23
Tartaric, U. S. P., cryst., bbls.	lb.	.23½
Tungstic, kegs	lb.	1.40
Valeric, c. p., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	2.56½
Amyl, from pentane, tanks	lb.	.143
Amyl, Imp. drums	gal.	1.75
Butyl, drums, c/l., wks.	lb.	.10½
Denatured, No. 5, comp. denat., c/l., drums	gal.	.34
Isoamyl, drums	gal.	4.00
Isobutyl, ref., drums	gal.	.75
Isopropyl, ref., drums	gal.	.50
Propyl, ref., drums	gal.	.75
Wood, *see* Methanol		
Alpha-naphthol, bbls.	lb.	.65
Alpha-naphthylamine, bbls.	lb.	.33

Alum, ammonia, lump, bbls., wks.	100 lbs.	3.00
Chrome, casks, wks.	100 lbs.	4.75
Potash, lump, bbls., wks.	100 lbs.	3.00
Soda, bbls., wks.	100 lbs.	4.00
Aluminum, metal, N. Y.	100 lbs.	22.90
Aluminum chloride, anhyd., commercial, wks., drums extra, c/l.	lb.	.04
Aluminum stearate, 100-lb. bbl.	lb.	.16
Aluminum sulfate, comm'l, bags, wks.	100 lbs.	1.25
Iron-free, bags, wks.	100 lbs.	1.90
Aminoazobenzene, 100-lb. kegs	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.15½
50,000-lb. tanks, wks.	lb.	.05
Ammonia, aqua, 26°, tanks, wks., contained NH_3	lb.	.05½
Ammonium acetate, kegs	lb.	.33
Bifluoride, bbls.	lb.	.15
Bromide, 50-lb. boxes	lb.	.35
Carbonate, tech., casks	lb.	.08
Chloride, gray, bbls.	100 lbs.	5.25
Lump, casks	lb.	.10½
Iodide, 25-lb. jars	lb.	4.30
Nitrate, tech., cryst., bbls.	lb.	.08½
Oxalate, kegs	lb.	.22
Persulfate, cases	lb.	.20
Phosphate, dibasic, tech., bbls.	lb.	.08½
Sulfate, bulk, wks.	ton	24.00
Amyl acetate, tech., from pentane, tanks, delivered	lb.	.135
Aniline oil, drums	lb.	.14½
Anthracene, 80–85%, casks, wks.	lb.	.75
Anthraquinone, subl., bbls.	lb.	.45
Antimony, metal	lb.	.07½
Antimony chloride, drums	lb.	.13
Oxide, bbls.	lb.	.08½
Salt, dom., bbls.	lb.	.22
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls.	lb.	.16
Vermilion, bbls.	lb.	.38
Argols, red powder, bbls.	lb.	.08
Arsenic, metal, kegs	lb.	.31
Red, kegs, cases	lb.	.13
White, c/l., kegs	lb.	.04
Asbestine, bulk, c/l.	ton	15.00
Barium carbonate, bbls., bags, wks.	ton	47.00
Chloride, bbls., wks.	lb.	.03¾
Dioxide, drs., wks.	lb.	.12
Hydroxide, bbls.	lb.	.05
Nitrate, casks	lb.	.07
Barium thiocyanate, 400-lb. bbls.	lb.	.27
Barytes, floated, 350-lb. bbls., wks.	ton	23.00
Benzaldehyde, tech., drums	lb.	.60
F. F. C., cbys.	lb.	1.40
U. S. P., cbys.	lb.	1.15
Benzidine base, bbls.	lb.	.65
Benzol, tanks, wks.	gal.	.22
Benzoyl chloride, drums	lb.	.40
Benzyl acetate, F. F. C., bottles	lb.	.75
Alcohol, drums	gal.	.75
Chloride, tech., drums	lb.	.30
Beta-naphthol, bbls.	lb.	.22
Beta-naphthylamine, bbls.	lb.	.58
Bismuth, metal, cases	lb.	1.05
Bismuth, nitrate, 25-lb. jars	lb.	.95
Oxychloride, boxes	lb.	2.95
Subnitrate, U. S. P., 25-lb. jars	lb.	1.25
Blanc fixe, dry, bbls.	ton	65.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, bags	lb.	.018
Bordeaux mixture, bbls.	lb.	.11½
Bromine, bot.	lb.	.36
Bromobenzene, drums	lb.	.50
Bromoform, jars	lb.	1.80
Butyl acetate, drums, c/l.	lb.	.11
Cadmium bromide, 50-lb. jars	lb.	1.25
Cadmium, metal, cases	lb.	.55

Cadmium sulfide, boxes	lb.	.60
Caffeine, U. S. P., 5-lb. cans	lb.	1.85
Calcium acetate, bags	100 lbs.	3.00
Arsenate, bbls	lb.	.07
Carbide, drums	lb.	.05½
Chloride, drums, wks., flake	ton	19.50
Cyanide, 100-lb. drums	lb.	.30
Nitrate, bags	ton	35.00
Phosphate, monobas., bbls	lb.	.07½
Tribas., bbls	lb.	.11
Calcium carbonate, tech., bags,	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl	lb.	.06½
Camphor, Jap., slabs	lb.	.50
Carbazole, bbls	lb.	.75
Carbon, activated, drums	lb.	.08
Carbon bisulfide, drums	lb.	.051
Carbon black	lb.	.0275
Carbon dioxide, liq. cyl	lb.	.06
Carbon tetrachloride, drums	lb.	.05¼
Casein, stand. gr., bbls	lb.	.14¾
Cellulose acetate, bbls	lb.	.80
Cerium oxalate, kegs	lb.	.25
Charcoal, willow, powd., bbls	lb.	.06
China clay, bulk	ton	8.00
Chloral hydrate, drums	lb.	.70
Chlorine, liq. c/l., cyl.*	lb.	.055
Chlorine, tanks	100 lbs.	1.75
Chlorobenzene, mono-, drums	lb.	.06
Chloroform, tech., drums	lb.	.20
Chromium acetate, 20° soln., bbls	lb.	.05
Coal tar, bbls., wks	bbl.	8.50
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls	lb.	1.15
Cod liver oil, bbls	bbl.	28.00
Copperas, c/l., bulk	ton	14.50
Copper, metal, elec	100 lbs.	8.75
Copper carbonate, bbls., 52/54%	lb.	.16¼
Chloride, bbls	lb.	.17
Cyanide, drums	lb.	.39
Oxide, red, bbls	lb.	.14¾
Sulfate, c/l., bbls	100 lbs.	3.75
Cotton, soluble, bbls	lb.	.40
Cream tartar, bbls	lb.	.17
Cyanamide, bulk, N. Y.	Ammonia unit	1.02½
Diaminophenol, kegs	lb.	3.80
Dianisidine, bbls	lb.	2.35
Dibutylphthalate, drums, wks	lb.	.20½
Diethylaniline, drums	lb.	.52
Diethylene glycol, drums	lb.	.14
Diethyl phthalate, drums	lb.	.23
Diethyl sulfate, tech., drums	lb.	.20
Dimethylaniline, drums	lb.	.26
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.18
Dinitrochlorobenzene, bbls	lb.	.13
Dinitronaphthalene, bbls	lb.	.34
Dinitrophenol, bbls	lb.	.23
Diphenylamine, bbls	lb.	.31
Diphenylguanidine, bbls	lb.	.30
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.70
Ether, nitrous, bot	lb.	.80
Ether, conc., drums	lb.	.09
Ethyl acetate, tanks, c/l	lb.	.07½
Bromide, drums	lb.	.50
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethylbenzylaniline, 300-lb. drums	lb.	.88
Ethylene chlorohydrin, anhyd. drums	lb.	.75
Glycol, c/l., wks	lb.	.26
Feldspar, bulk	ton	6.50
Ferric chloride, tech., bbls	lb.	.05
Ferrous chloride, cryst., bbls	lb.	.06
Ferrous sulfide, bbls	100 lbs.	2.50
Fluorspar, 98%, bags	ton	31.00
Formaldehyde, bbls	lb.	.06
Formaniline, drums	lb.	.37½
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural, drums, tech., contract, works	lb.	.10
Glauber's salt, bbls	100 lbs.	1.00
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerine, C. P., drums	lb.	.10¼
G salt, bbls	lb.	.42
Hexamethylenetetramine, tech., drums	lb.	.46
Hydrogen peroxide, 25 vol., bbls	lb.	.05½
Hydroquinone, kegs	lb.	1.20
Indigo, 20%, paste, bbls	lb.	.12
Iodine, crude, 200-lb. kgs	kilo	£1 5s
Iodine, resubl., jars	lb.	3.35
Kieselguhr, bags	ton	50.00
Lead, metal, N. Y.	100 lbs.	4.50
Lead acetate, bbls., white	lb.	.11
Arsenate, bbls	lb.	.10
Oxide, litharge, bbls	lb.	.07
Peroxide, drums	lb.	.20
Red, bbls	lb.	.08
Sulfate, bbls	lb.	.06
White, basic carb., bbls	lb.	.06½
Lime, hydrated, bbls	100 lbs.	.85
Lime, live, chemical, bbls., wks.,	280 lbs.	1.70
Limestone, ground, bags, wks	ton	4.50
Lithopone, bbls	lb.	.04½
Magnesite, crude	ton	32.00
Calcined, 500-lb. bbls., wks	ton	46.00
Magnesium, metal, wks	lb.	.30
Magnesium carbonate, bags	lb.	.05¼
Chloride, drums	ton	36.00
Fluosilicate, cryst., bbls	lb.	.10
Oxide, U. S. P., light, bbls	lb.	.42
Manganese chloride, casks	lb.	.07½
Dioxide, 80%, bbls	ton	80.00
Sulfate, casks	lb.	.09
Mercury bichloride, cryst., 100 lbs.	lb.	.77
Mercury flasks, 76 lbs	flask	64.00
Meta-nitroaniline, bbls	lb.	.67
Meta-phenylenediamine, bbls	lb.	.82
Meta-tolylenediamine, bbls	lb.	.67
Methanol, pure, synthetic, drums, delivered	gal.	.37½
Tanks, delivered	gal.	.35½
Methyl acetone, drums	gal.	.54
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.45
Michler's ketone, bbls	lb.	2.50
Naphthalene, flake, bbls	lb.	.04¾
Nickel, metal	lb.	.35
Nickel salt, single, bbls	lb.	.12
Double, bbls	lb.	.12
Niter cake, bulk	ton	11.50
Nitrobenzene, drums	lb.	.08½
Oil, castor, No. 1	lb.	.10¼
China wood, bbls	lb.	.07¾
Coconut, Ceylon, tanks	lb.	.03
Cod, N. F., bbls	gal.	nom.
Corn, crude, tanks, mills	lb.	.05⅛
Cottonseed, crude, tanks	lb.	.04
Lard, edible, bbls	lb.	.08
Linseed, bbls	lb.	.109
Menhaden, crude, tanks	gal.	.17
Neat's-foot, pure, bbls	lb.	.14
Oleo, No. 1, bbls	lb.	.06⅞
Olive oil, denat., bbls	gal.	.72
Foots, bbls	lb.	.06
Palm, Lagos, casks	lb.	.04½
Peanut, crude, tanks	lb.	.05
Perilla, bbls	lb.	.09⅞
Rapeseed, bbls	gal.	.68
Red, bbls	lb.	.07
Soy bean, crude, tanks	lb.	.080
Sperm, 38°, bbls	lb.	.103
Whale, bbls., natural, winter	lb.	.072
Ortho-aminophenol, kegs	lb.	2.15
Ortho-dichlorobenzene, drums	lb.	.08
Ortho-nitrochlorobenzene, drums	lb.	.28
Ortho-nitrophenol, bbls	lb.	.85
Ortho-nitrotoluene, drums	lb.	.16
Ortho-toluidine, bbls	lb.	.14½
Para-aminophenol, kegs	lb.	.78
Para-dichlorobenzene	lb.	.15½
Para-formaldehyde, cases	lb.	.38
Paraldehyde, tech., drums	lb.	.20½
Para-nitraniline, drums	lb.	.48
Para-nitrochlorobenzene, drums	lb.	.25
Para-nitrophenol, bbls	lb.	.45
Para-nitrosodimethylaniline, bbls	lb.	.92
Para-nitrotoluene, bbls	lb.	.29
Para-phenylenediamine, bbls	lb.	1.15
Para-toluidine, bbls	lb.	.58
Paris Green, 250-lb. kegs	lb.	.23
Phenol, drums	lb.	.14¼
Phenolphthalein, drums	lb.	.52
Phenylethyl alcohol, 1-lb. bot	lb.	3.75
Phosphorus, red, cases	lb.	.45
Phosphorus trichloride, cyl	lb.	.18
Phthalic anhydride, bbls	lb.	.15
Platinum, metal	oz.	24.00
Potash, caustic, drums	lb.	.07¼
Potassium acetate, kegs	lb.	.27
Bicarbonate, casks	lb.	.07½
Bichromate, casks	lb.	.07⅝
Binoxalate, bbls	lb.	.14
Bromide	lb.	.31
Carbonate, 80–85%, calc., casks	lb.	.06¾
Chlorate, kegs	lb.	.09
Chloride, crystals, bbls	lb.	.04¾
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls	lb.	.10½
Muriate, fert., bulk	ton	35.55
Permanganate, drums	lb.	.17½
Prussiate, red, casks	lb.	.35
Yellow, casks	lb.	.16½
Titanium oxalate, bbls	lb.	.21
Pyridine, drums	gal.	.85
Resorcinol, tech., kegs	lb.	.65
Rochelle salt, bbls., U. S. P.	lb.	.11½
R salt, bbls	lb.	.40
Saccharin, cans	lb.	1.70
Salt cake, bulk	ton	13.00
Saltpeter, gran., bbls	lb.	.05¾
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot	oz.	.26¼
Soda ash, 58%, light, bags, contract, wks	100 lbs.	1.20
Soda, caustic, 76%, solid, drums, contract, wks	100 lbs.	2.55
Sodium acetate, bbls	lb.	.05
Benzoate, bbls	lb.	.42
Bicarbonate, bbls	100 lbs.	1.85
Bichromate, casks	lb.	.05
Bisulfite, bbls	lb.	.02¾
Bromide, bbls., U. S. P.	lb.	.31
Chlorate, kegs	lb.	.05¾
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.15½
Fluoride, bbls	lb.	.07½
Metallic, drums, $12^{1}/_{4}$-lb. bricks	lb.	.19
Metasilicate, cryst	100 lbs.	3.25
Metasilicate, gran., bbls	100 lbs.	2.65
Naphthionate, bbls	lb.	.52
Nitrate, crude, 200-lb. bags, N. Y.	100 lbs.	1.26
Nitrite, bbls	lb.	.07¼
Perborate, bbls	lb.	.17
Peroxide, cases	lb.	.21
Phosphate, trisodium, bbls	100 lbs.	2.50
Phosphate, disodium, bags	100 lbs.	2.00
Picramate, kegs	lb.	.67
Prussiate, bbls	lb.	.11½
Silicate, drums, tanks, 40°	100 lbs.	.75
Silicofluoride, bbls	lb.	.04¾
Stannate, drums	lb.	.29½
Sulfate, anhyd., bbls	lb.	.02
Sulfide, cryst., bbls	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls	lb.	.30
Thiosulfate, reg., cryst., bbls	lb.	.02½
Tungstate, kegs	lb.	.65
Strontium carbonate, tech., bbls	lb.	.07¼
Nitrate, bbls	lb.	.09
Sulfur, bulk, mines, wks	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
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Thiocarbanilid, bbls	lb.	.25
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Tribromophenol, cases	lb.	1.10
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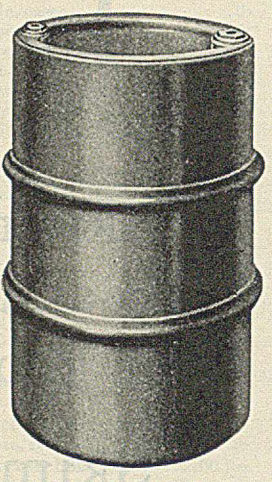

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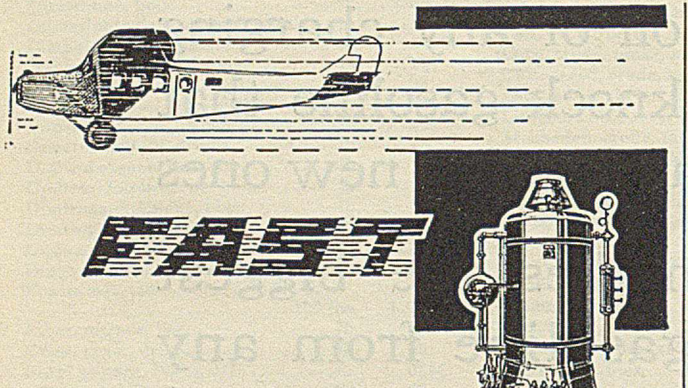

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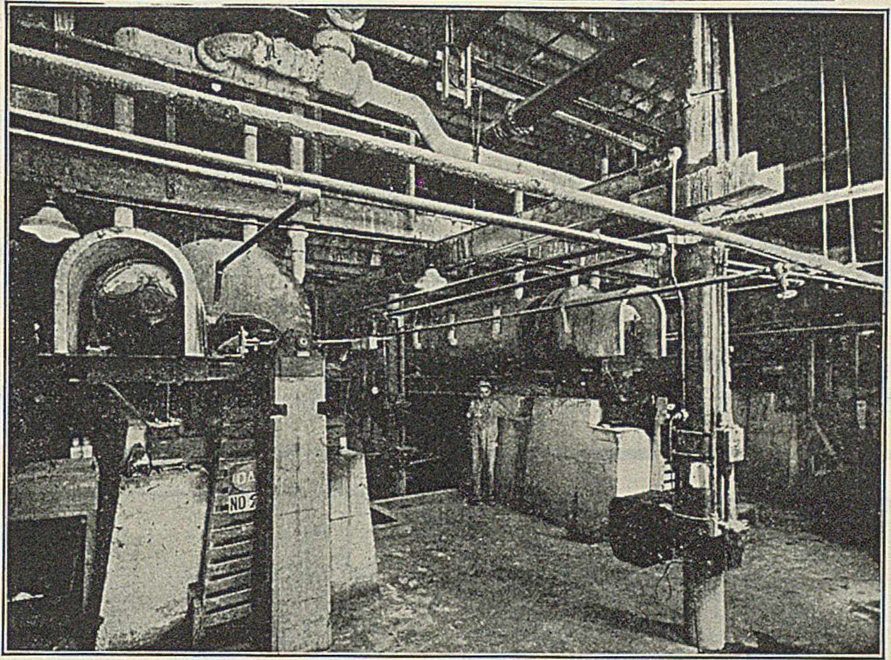

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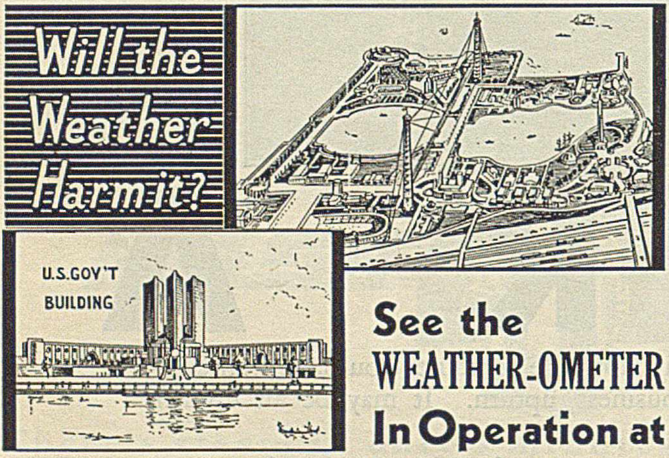

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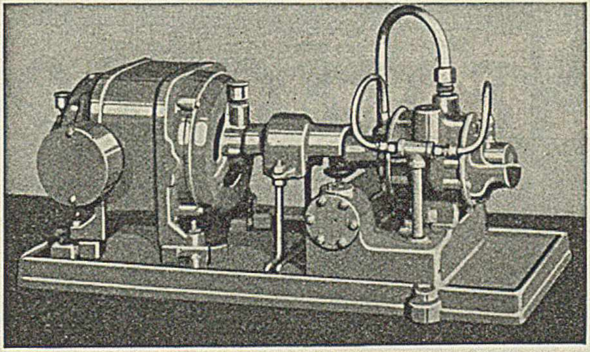

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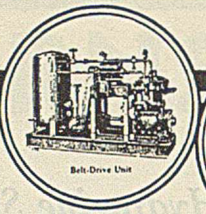
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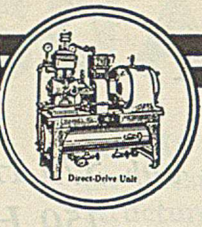
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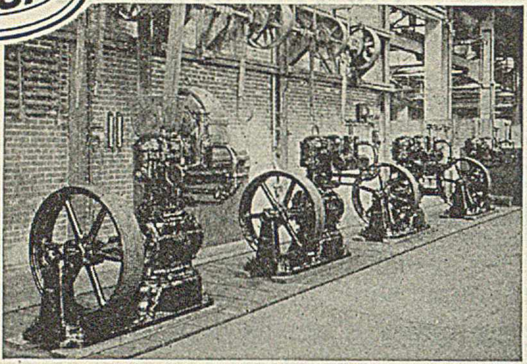
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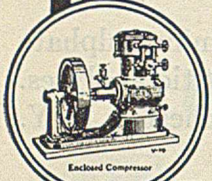
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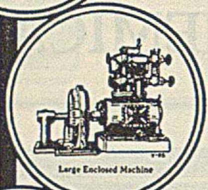
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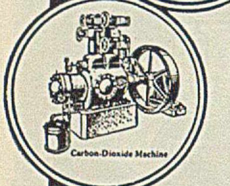
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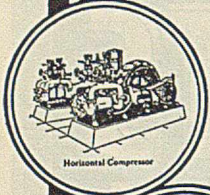
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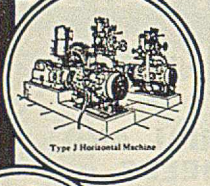
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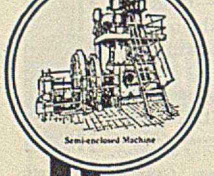
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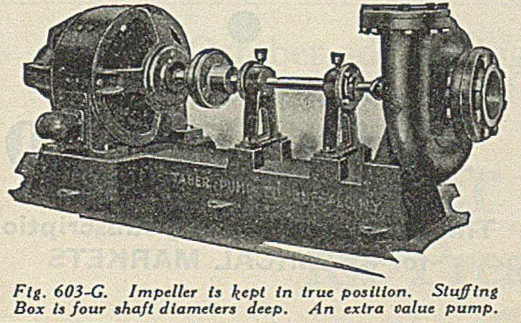

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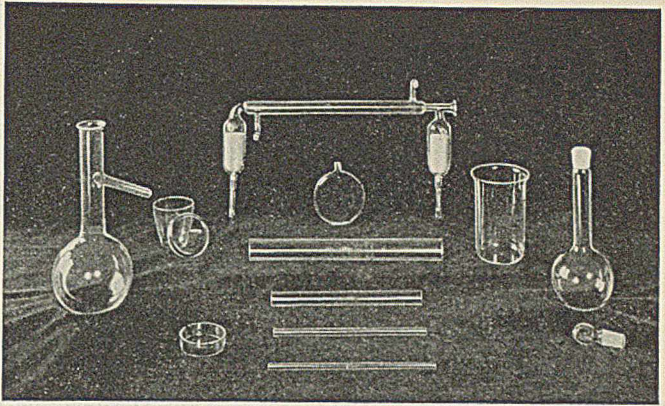

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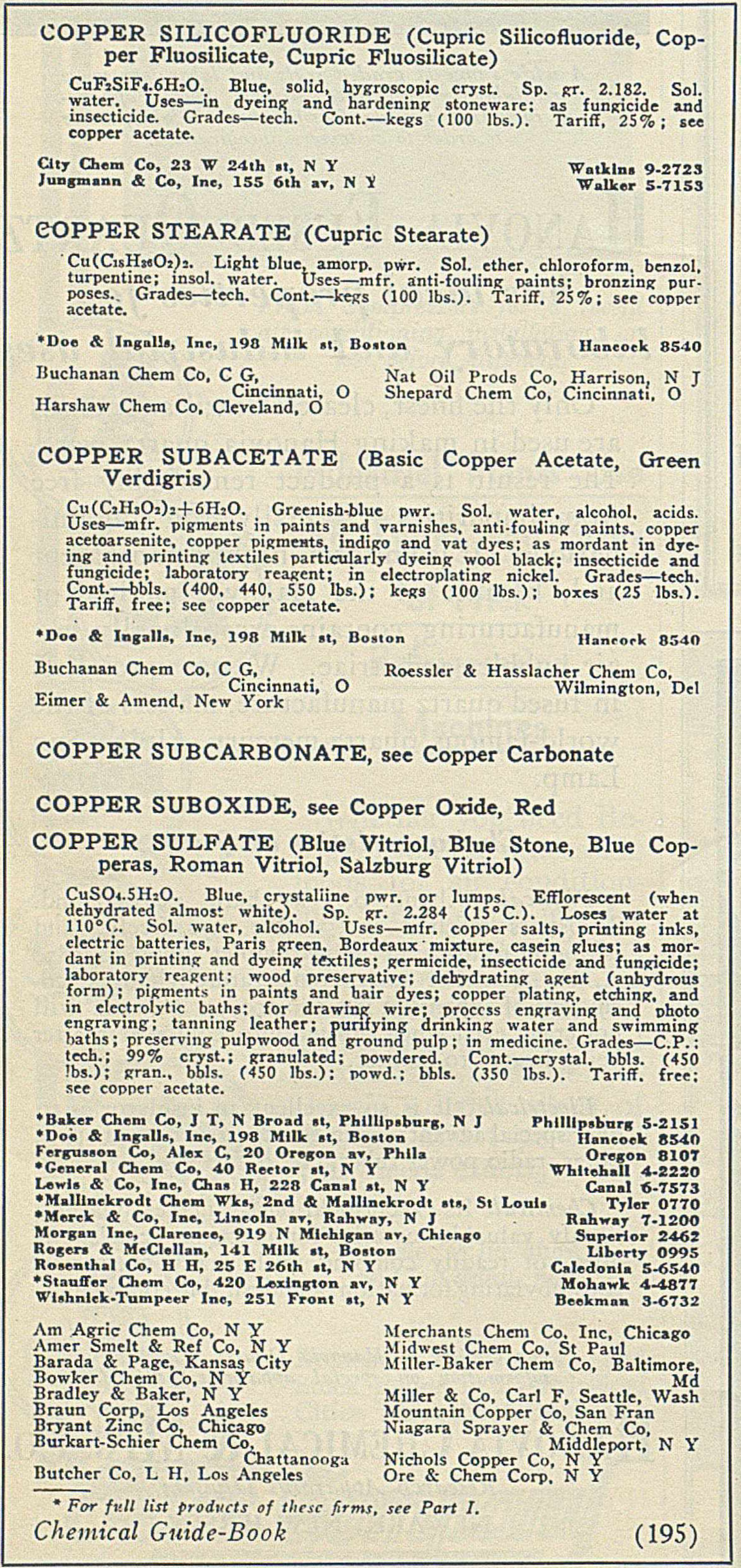

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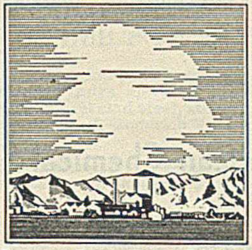

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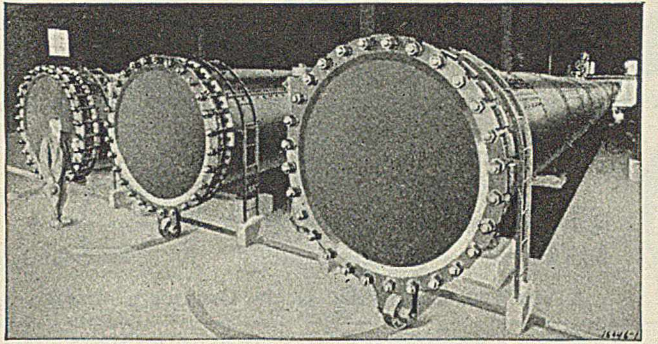

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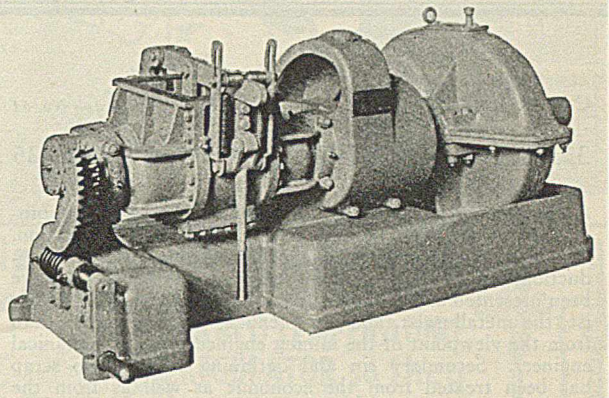

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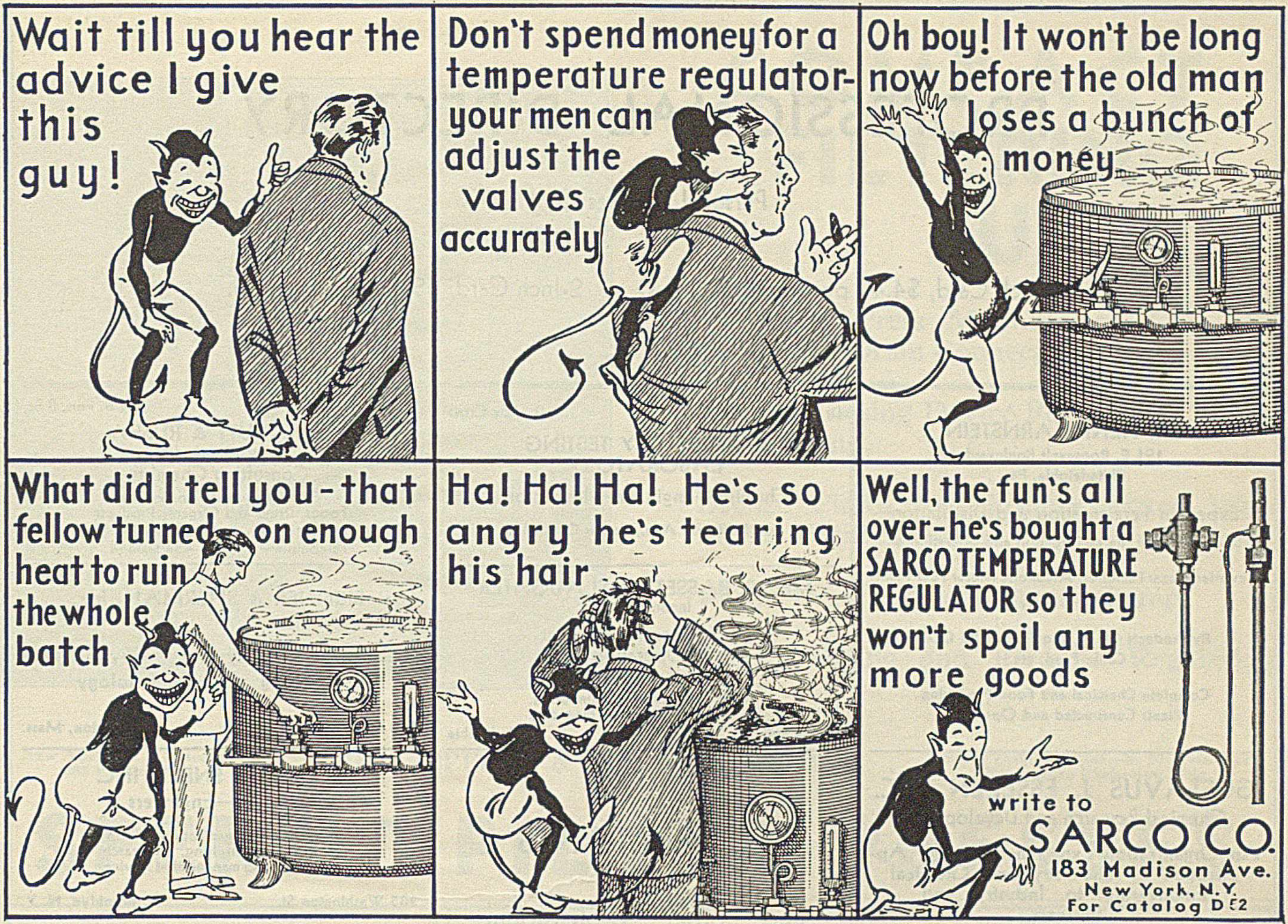
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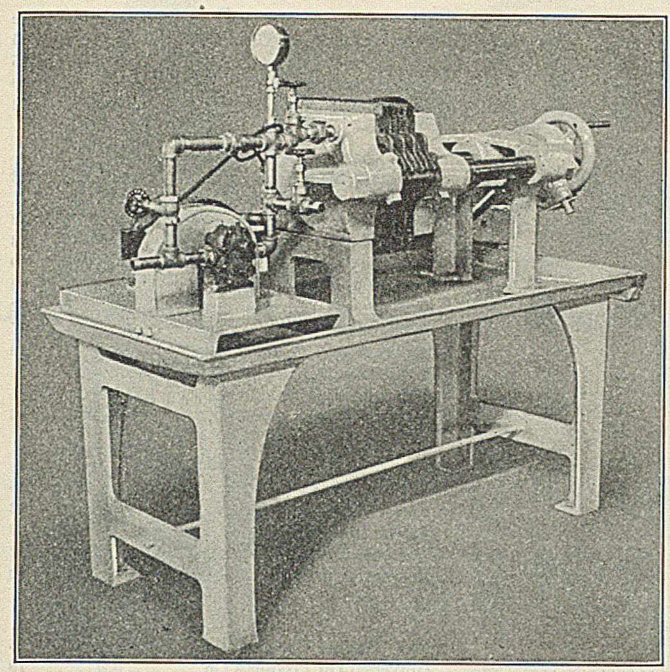

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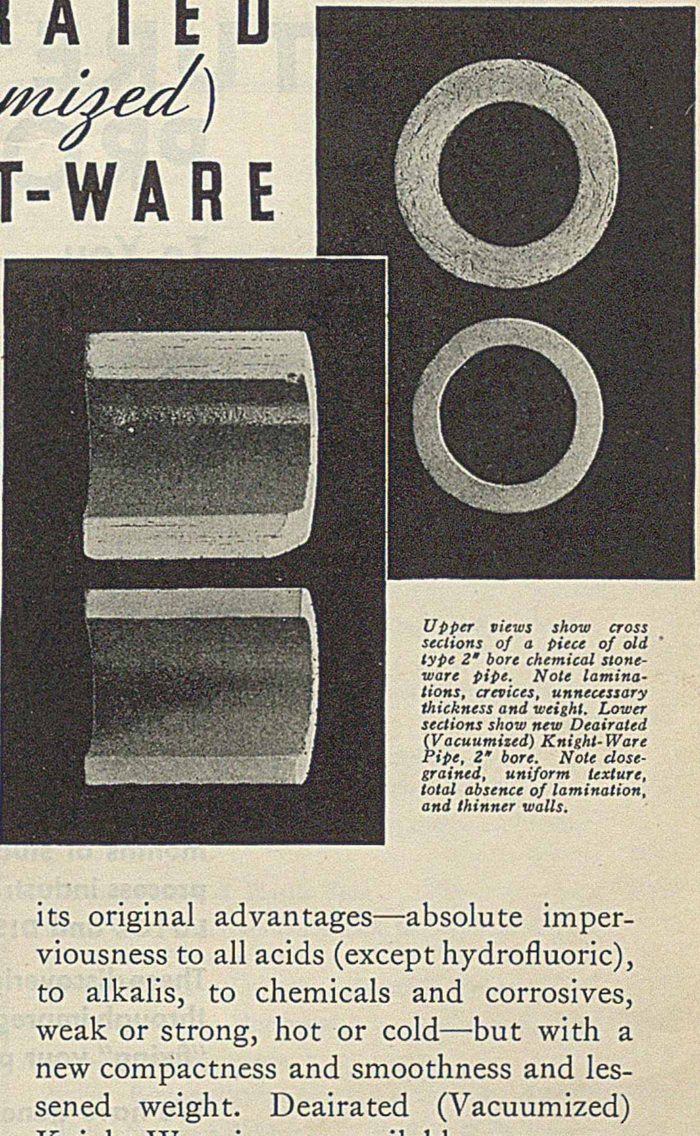

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