INDUSTRIAL
EDITION
VOL. 26, No. 3

March, 1934

Industrial AND ENGINEERING Chemistry

VOL. 26, CONSECUTIVE NO. 8

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

PUBLICATION OFFICE: Easton, Pa.
EDITORIAL OFFICE:
Room 706, Mills Building,
Washington, D. C.
TELEPHONE: National 0848
CABLE: Jiechem (Washington)

ADVERTISING DEPARTMENT:
332 West 42nd St.,
New York, N. Y.
TELEPHONE: Bryant 9-4430

CONTENTS

16,000 Copies of This Issue Printed

Subscription to nonmembers, $7.50; single copy, 75 cents, to members, 60 cents. Foreign postage $2.10, except to countries accepting mail at American domestic rates and to Canada, 70 cents. Subscriptions, changes of address, and claims for lost copies should be referred to Charles L. Parsons, Secretary, Mills Building, Washington, D. C. The Council has voted that no claims will be allowed for copies of journals lost in the mails, unless such claims are received within 60 days of the date of issue, and no claims will be allowed for issues lost as a result of insufficient notice of change of address. (Ten days' advance notice required.) "Missing from files" cannot be accepted as the reason for honoring a claim. If change of address implies a change in position, please indicate its nature.

The AMERICAN CHEMICAL SOCIETY also publishes the *Journal of the American Chemical Society* and *Chemical Abstracts.*

NATIONAL · ANILINE

Industrial Chemicals

A comprehensive line of Coal-Tar Derivatives serving the following industries ◆ Dyestuff ◆ Textile (Wetting-out Agents) ◆ Synthetic Resin ◆ Paint ◆ Lacquer (Solvents and Plasticizers) ◆ Mining (Flotation Re-agents) ◆ Wood Preservation ◆ Insecticide ◆ Germicide ◆ Rubber (Accelerators and Anti-Oxidants) ◆ Gasoline and Oil (Inhibitors) ◆ Steel (Inhibitors) ◆ Explosive ◆ Pharmaceutical.

Alpha Naphthol
Alpha Naphthylamine
Amino Naphthol Sulphonic Acid (1:2:4)
Amino Azo Benzene Hydrochloride
Amino Azo Toluene Base
Amino G Salt
Amino H Acid
Amino J Acid
Amino Phenol Sulphonic Acid (1:2:5)
Aniline Oil
Anthraquinone
Anthrarufin

Benzanthrone
Benzidine Base-Distilled
Benzoyl Benzoic Acid (Ortho)
Beta Amino Anthraquinone
Beta Naphthol
Beta Naphthylamine
Broenners Acid

Calcium Malate (Normal)
Cassella Acid
Chicago Acid (SS Acid)
Chlor Benzanthrone
Chlor Quinizarine
Chromotropic Acid
Cleves Acid (1:6–1:7 & Mixed)
Cumidine

Dianisidine
Diethyl Aniline
Dimethyl Aniline
Dinitrobenzene
Dinitrochlorobenzene
Dinitrotoluene (M. P. 66° — 55° — 20°)
Dinitrotoluene Oily
Dinitrophenol
Dinitrostilbene Disulphonic Acid
Di-Ortho-Tolyl Thiourea

Diphenyl Methane
Ditolyl Methane

Epsilon Acid
Ethyl Benzyl Aniline
Ethyl Benzyl Aniline Sulphonic Acid

Fumaric Acid

G-Salt
Gamma Acid

H-Acid
Hydroquinone

Isatin

J-Acid

Koch Acid

L-Acid
Laurents Acid

Malic Acid
Maleic (Toxilic) Acid
Maleic (Toxilic) Anhydride
Metanilic Acid
Meta Nitro Para Toluidine
Meta Phenylene Diamine & Sulpho Acid
Meta Toluylene Diamine & Sulpho Acid
Mixed Toluidine
Myrbane Oil

Neville-Winthers Acid
Nitro Amino Phenol (4:2:1)
Nitro Benzene
Nitroso Phenol (Para)

Ortho Anisidine
Ortho Chlor Benzaldehyde
Ortho Chlor Benzoic Acid

Ortho Chlor Toluene
Ortho Nitro Anisole
Ortho Nitro Toluene
Ortho Toluidine

Para Amino Phenol
Para Amino Acetanilide
Para Nitroaniline
Para Nitrotoluene
Para Nitroso Dimethylaniline
Para Toluidine
Peri Acid
Phenyl J. Acid
Phenyl Peri Acid
Phthalic Anhydride

Quinizarine

R-Salt

S-Acid
SS-Acid (Chicago Acid)
Schaeffer Salt
Schoellkopf Acid
Sodium Hydrosulfite
Sodium Metanilate
Sodium Naphthionate
Sodium Sulphanilate
Succinic Acid
Sulphanilic Acid

Tetra Chlor Phthalic Anhydride
Thiocarbanilide
Tobias Acid
Tolidine
Tolazine
Tolyl Peri Acid
Triphenylguanidine

Xylidine

NATIONAL ANILINE & CHEMICAL COMPANY, INC.
(Intermediates Division) *(Bowling Green 9-2240)*
40 Rector Street New York City

NATIONAL N DYES

INTERMEDIATES

Published by the American Chemical Society, Publication Office, 20th & Northampton Sts., Easton, Pa.
Entered as second-class matter at the Post-Office at Easton, Pa., under the Act of March 3, 1879, as 42 times a year. Industrial Edition monthly on the 1st; News Edition on the 10th and 20th; Analytical Edition bimonthly on the 15th.
Acceptance for mailing at special rate of postage provided for in Section 1103, Act of October 3, 1917, authorized July 13, 1918.

THE LISTENING POST

Rancidity of Fats caused by oxidation may be postponed by adding minute quantities of certain inhibitors. The relative values of various inhibiting compounds have been studied by Greenbank and Holm (page 243), who have shown that maleic acid ranks in effectiveness with some of the phenols.

Light, as well as oxygen, affects the development of rancidity, and Coe and LeClerc (page 245) have investigated the effects of various light filters on this phenomenon, showing that green light is safest.

Fundamental Thermal Data for fats and fatty acids are given by Mills and Daniels (page 248) for the assistance of the chemical engineer in designing fatty-acid stills for greater efficiency.

Treatment of Water Supplies to effect economies in its general use has been studied by Hopkins, Armstrong, and Baylis (page 250). The savings to be made by communities (using water of a hardness not greater than 75 parts per million) by proper treatment of the raw water have been calculated on the basis of results achieved in Baltimore, and the findings are applicable generally to municipal water supplies.

Water Softening saves corrosion of mains and hence may effect major economies in amortization of plant, according to Powell (page 254), without affecting potability.

Potash from Georgia Shale with aluminum oxide as a salable by-product may assist in providing this essential fertilizer constituent for our farmers. Madorsky (page 256) presents a possible method of recovering it.

Sensitivity of Hydrocarbons to Heat, even during the short period of the explosion in an internal combustion engine, may profoundly affect the nature of the explosion reactions. Rice (page 259) contributes data on the cracking of the compounds present in gasoline to the solution of the detonation problem.

Progress in the Utilization of petroleum hydrocarbons as raw materials for chemical industry will probably be made by the discovery and development of direct reactions which avoid the cumulative losses of steplike processes. Wiezevich and Frolich (page 267) contribute a study of the direct catalytic oxidation of hydrocarbons with air, and not only give us the benefit of a large number of experiments but also include a lengthy bibliography. Although no process yet commercially satisfactory is described, much of the fundamental knowledge on which such a practical result will be based is included in their discussion.

Drying Chrome Leather, important in arresting the reactions of tanning at the proper point, has in the past been conducted as a batch operation which is both expensive and in some respects uncertain. Continuous tunnel drying is being developed for this industry as a substantial improvement in many ways. Hougen (page 333) has investigated the drying characteristics of skins and provides fundamental data for the design of such continuous driers.

Among the Most Important Characteristics of cellulosic materials is their behavior with water. Sheppard and Newsome (page 285) have looked into this and supply interesting and important data on the ways in which water can attach itself to cellulose to affect its properties.

How Does Solid Matter affect boiler operation, is the question Foulk and Whirl (page 263) have set themselves. In this second article on the subject they show that suspended solids lose their foam-stabilizing tendencies at high temperatures and pressures.

Silicate of Soda as an added ingredient in soap at one time was the subject of vigorous argument between those who thought it valuable and others who considered it useless. Careful study and long experience indicate definitely that it is useful in many ways as a detergent. Carter and Stericker (page 277) have studied its effect on soap and report findings of value to soap makers.

Academic Research often fails in its full usefulness because the conditions chosen for study are quite impossible or impracticable to realize in industry. Countless examples of beautifully planned and executed researches which fail to be valuable through lack of appreciation of industrial conditions are familiar to everyone. Frary (page 281) is eminently qualified to suggest the landmarks and guide lines to be observed in planning academic metallurgical research to make it useful, and this he does in his paper on metals and alloys.

Orange Juice is one of the most fragile materials in the ordinary diet and many methods of preserving it have been proposed to relieve the cook of having to prepare it fresh for every breakfast. Joslyn and Marsh (page 295) have studied the effect of freezing storage on its various properties and here report findings.

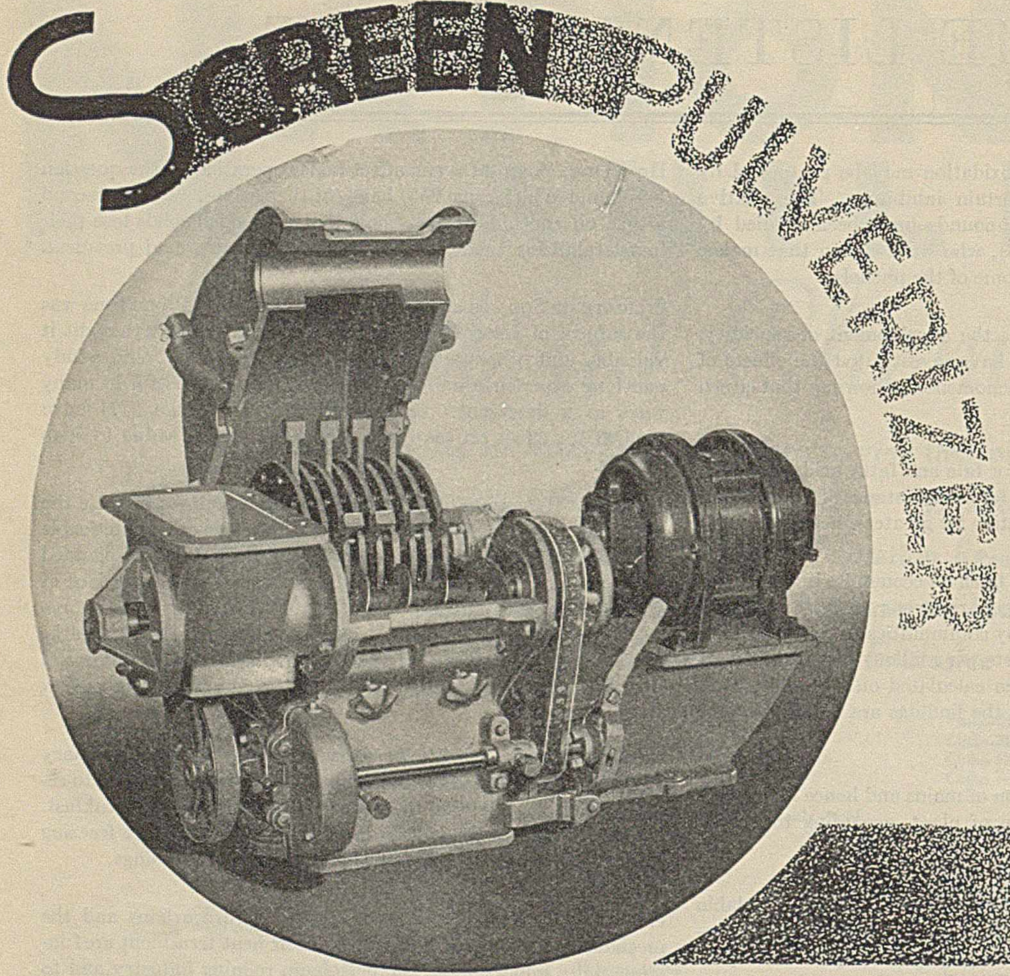
Cracking Characteristics of gaseous hydrocarbons and the mechanism of reactions initiated by their heat treatment are fundamentally important to the petroleum refining industry and to the utilization of this potential source of raw materials for organic synthesis. Dunstan, Hague, Wheeler, and Cadman (pages 307 and 315) have gone into this subject experimentally in considerable detail on both laboratory and plant scales and report their findings. Their paper deserves, and will no doubt receive, close attention from the petroleum industry as well as from organic chemists generally.

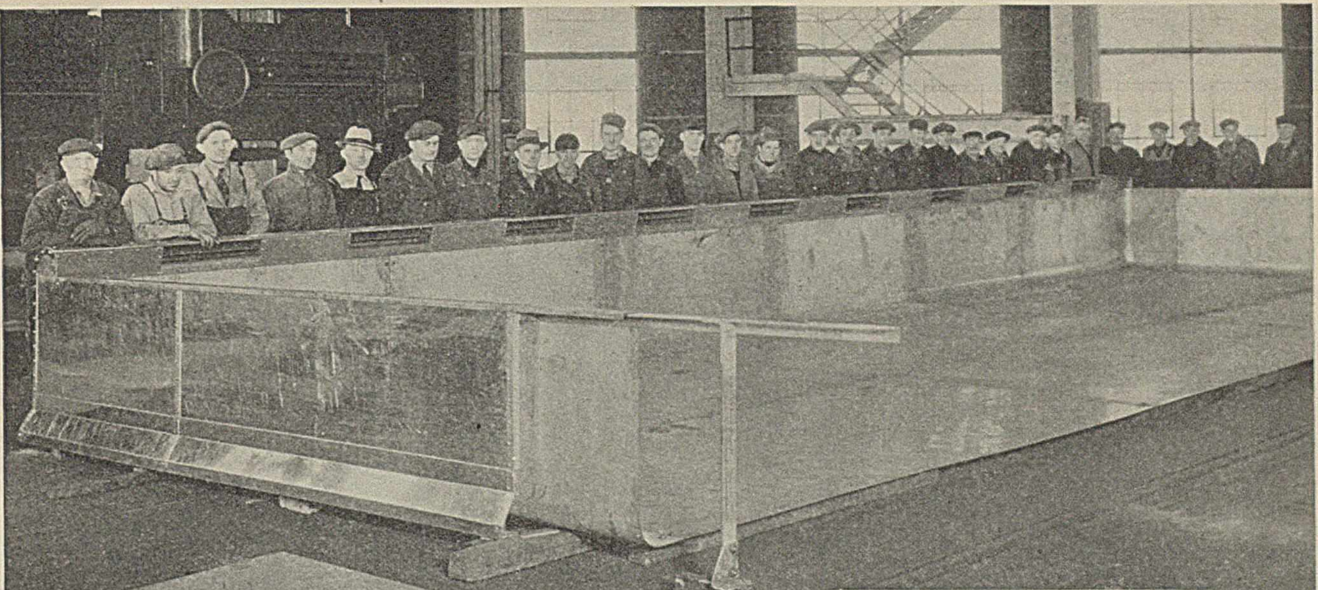
Physical Factors fundamental to cracking petroleum and the design of cracking plants are evaluated by Brown, Lewis, and Weber (page 325).

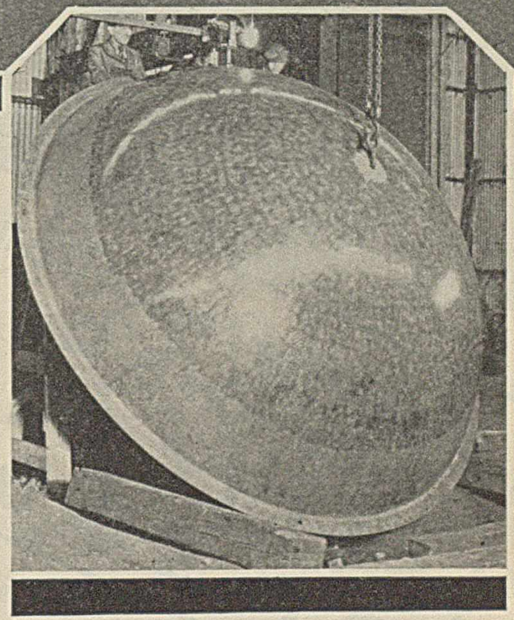
Sulfur Fungicides possessing the toxicity of sulfur itself undiminished and at the same time endowed with the colloidal properties of bentonite have proved to be extremely valuable in use. McDaniel (page 340) describes these interesting compounds and the method of their manufacture by fusing sulfur into the structure of bentonite clay. To one unfamiliar with the colloidal properties of this important earth, the finished material is the more remarkable since one might expect the sulfur fusion to destroy or materially modify its unique characteristics.

Business in Chemical Products is definitely on the upturn, according to Wilson (page 351), who analyzes foreign trade during the past year in comparison with 1932. Although trade is far below what we hope will be normal, the definiteness of improvement and the indications of the first effects of business revival are unmistakable. Perhaps the most striking fact in the situation is that both imports and exports are increasing despite the vagaries of money during the period.

A Newly Determined Table of the refractive index of pure glycerol, values of prime importance in the soap and glycerol industry, is given by Hoyt (page 329).


SCREEN PULVERIZER





COPPERSMITHING *that keeps pace with modern* INDUSTRIAL REQUIREMENTS

TWENTY-FIVE thousand gallons of material in every batch will be cooled and processed in the special all copper pan, only half of which is shown in the larger illustration. Over seven thousand rivets hold the twelve tons of copper sheets rigidly and securely in place. The inside is perfectly smooth—even the seams and corners; to meet the exacting sanitary requirements of the food product to be handled. Every part of the fifteen hundred square foot bottom is flat, because thorough drainage is important.

The largest dished copper bottom ever *built in one-piece* is shown in the other illustration. It is slightly more than 14′ in diameter and weighs over two tons. The sheet has been worked to a depth of 51″; and still the metal is uniform in thickness.

When your design calls for coppersmithing, or it is needed for replacement—no matter what the industrial application is, why not let BUFLOVAK assume the responsibilities for you? Here you will find engineering talent and modern manufacturing facilities ideally combined to quickly and satisfactorily complete your assignment.

BUFFALO FOUNDRY & MACHINE CO.
1549 Fillmore Ave., BUFFALO, N. Y.

NEW YORK
295 Madison Ave.

CHICAGO
1636 Monadnock Bldg.

ST. LOUIS
2217 Olive St.

SAN FRANCISCO, 972 Russ Bldg.

In Canada: BUFLOVAK COMPANY OF CANADA, LIMITED, 1101 Canada Permanent Bldg., Toronto

BUFLOVAK
Reg. Trade Mark

BREWHOUSE EQUIPMENT
DISTILLATION APPARATUS
*DRYERS
*EVAPORATORS
*IMPREGNATORS
*FUMIGATORS
*VULCANIZERS
*CHEMICAL PLANT EQUIPMENT
CHEMICAL CASTINGS

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

ON THE SMOOTH ENAMELED TABLE TOP

Discover another use for P. Q. SILICATE OF SODA

THE LADY OF THE HOUSE knows the "acid test" for enameled ware. "Will it stand lemon juice?" she asks. When P. Q. Silicate is used in the enameler's formula, it will.

Greater acid resistance of cooking utensils, sinks, gas ranges, etc., results with the aid of the proper grade of P. Q. Silicate of Soda. Important benefits from the silicate in the enamel include a reduced smelting time and a greater effect from expensive opacifiers.

Other industries also find need for P. Q. Silicate in various protective coatings. The oil cracking plant for instance uses a coating for steel reaction chambers in which silicate is an essential ingredient. Here the metal is protected from corrosive substances and gases.

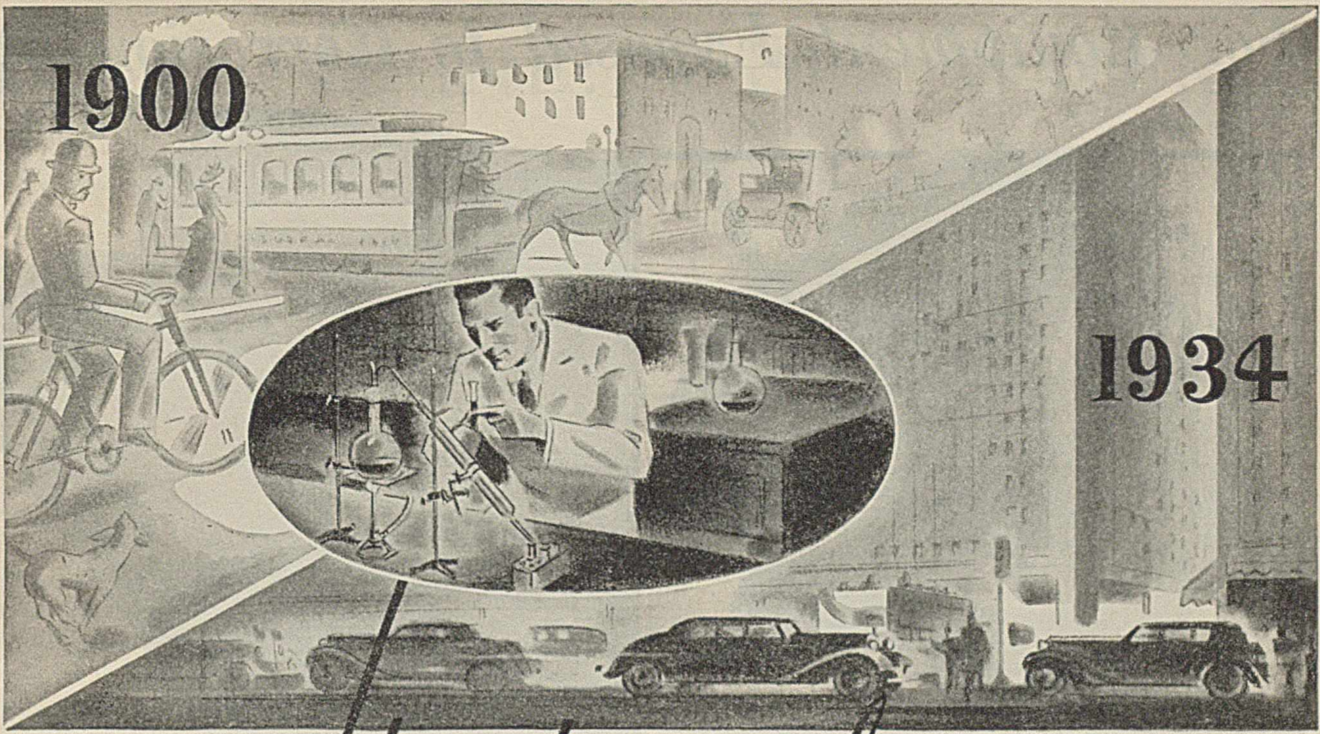
Your process may require a similar effective, economical coating. Our Technical Department will co-operate in any research you may undertake to use P. Q. Silicate in your plant. We'll be glad to suggest the places where you might use it.

General Offices and Laboratory: 125 S. Third St., Philadelphia, Penna. Chicago Sales Office: 205 W. Wacker Drive. Stocks in 65 cities. Sold in Canada by NATIONAL SILICATES LTD., Toronto, Ontario.

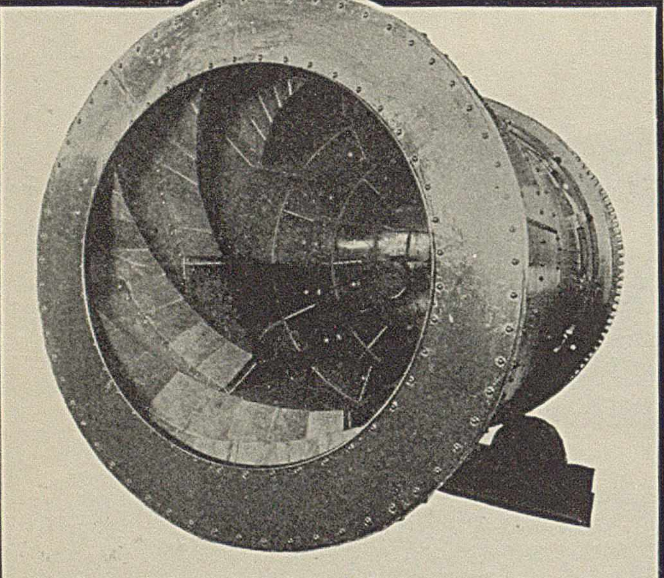
Works: Anderson, Ind., Baltimore, Md., Chester, Pa., Buffalo, N.Y., Kansas City, Kans., Rahway, N. J., St. Louis, Mo., Utica, Ill.

PHILADELPHIA QUARTZ COMPANY

EST. 1831

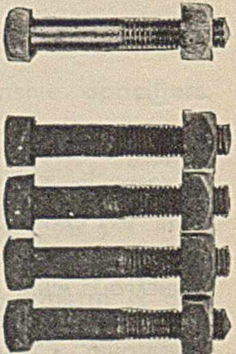

1900
1934

For Equipment Exposed to Corrosion by

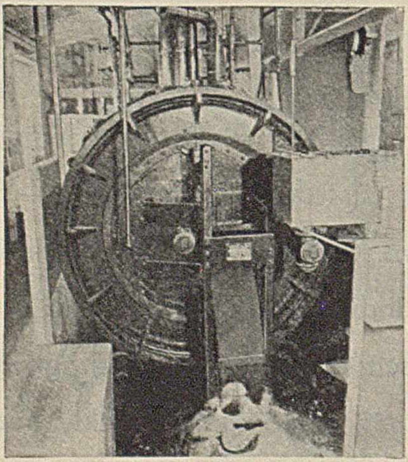


• *Feed end of one of two large, oil-fired rotary salt dryers with Monel Metal linings and flights. These dryers are 66" dia. x 40 ft. long and were built by C. O. Bartlett & Snow Co., Cleveland, Ohio, for one of the plants of the International Salt Co.*

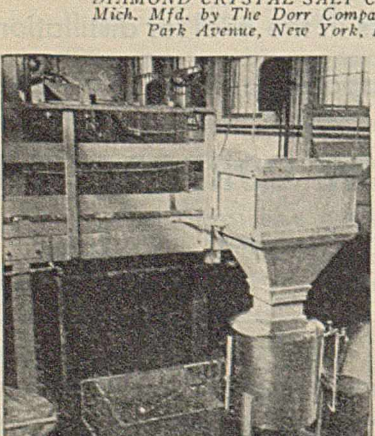
• (ABOVE) *All Monel Metal salt washing hopper built by L. O. Koven & Bro., Inc., Jersey City, N. J. for a well-known salt company. Salt Crystals are washed with a saturated brine solution.*



• (ABOVE) *Monel Metal Bolts used in contact with the polluted salt water of the Kill von Kull for fastening intake lines and condenser coils. 50,000 of these bolts were installed in 1910. A few of them were removed for examination in 1932 after continuous service and found to be in the same condition as when first placed in service. Top bolt has been cleaned, shows no evidence of corrosion.*

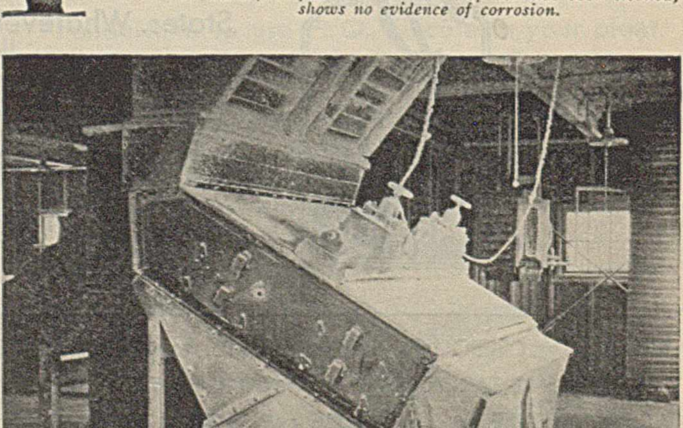


• *Monel Metal filter cloth is used as the filter medium on this "DORRCO" filter in plant of DIAMOND CRYSTAL SALT CO., St. Clair, Mich. Mfd. by The Dorr Company, Inc., 247 Park Avenue, New York, N. Y.*



• (RIGHT) *Close-up of one of the Hum-mer Monel Metal Salt Screens in use at the Kleer Salt Mine (Morton Salt Company), Grand Saline, Texas. Manufactured by W. S. Tyler Co., Cleveland, Ohio.*

• (LEFT) *Monel Metal Rock Salt DISSOLVER and Monel Metal Brine Supply Tank at one of the DuPont plants. These tanks are supplied by the INTERNATIONAL SALT CO., INC. to users of ISCO Rock Salt. This unit is capable of producing 100 gallons of saturated brine per hour. Larger units are built of Nickel-Clad Steel.*



SALT . . . BRINE . . . *or* SEA WATER . . .

use Monel Metal . . .

it stands up!

EQUIPMENT that handles salt, or is in contact with brine or sea water, must . . . as chemical engineers know from experience . . . be made of unusually resistant material.

In *all* these applications, the first demand is for immunity from rust, and a high degree of resistance to corrosion.

Equally as important, in many installations, are toughness and strength.

Wherever salt crystals are handled there is an imperative need of ability to withstand abrasion in the presence of constant, grinding wear.

And in a large number of plants, freedom from metallic reaction is imperative . . . to avoid contaminating or discoloring the product.

Monel Metal is the outstanding commercial metal that combines ALL these qualities: absolute rust-proofness, stubborn resistance to corrosion, strength equal to that of steel, extreme toughness, ability to withstand severe abrasion, and the mechanical and chemical stability that assures the complete purity of the product handled.

Salt-making service, severe

For more than 25 years, Monel Metal has been used in many different kinds of salt refining equipment, and in installations that are exposed to brine. Pure Nickel and Nickel-Clad Steel have also found many uses.

A roster of the users of Monel Metal-lined salt dryers is a blue book of the salt refining industry.

One of the most severe types of service is that of aprons on salt grainers, where Monel Metal is subjected to a set of corrosion-accelerating conditions that include abrasion, temperature, moisture, and complete aeration.

Interesting new developments

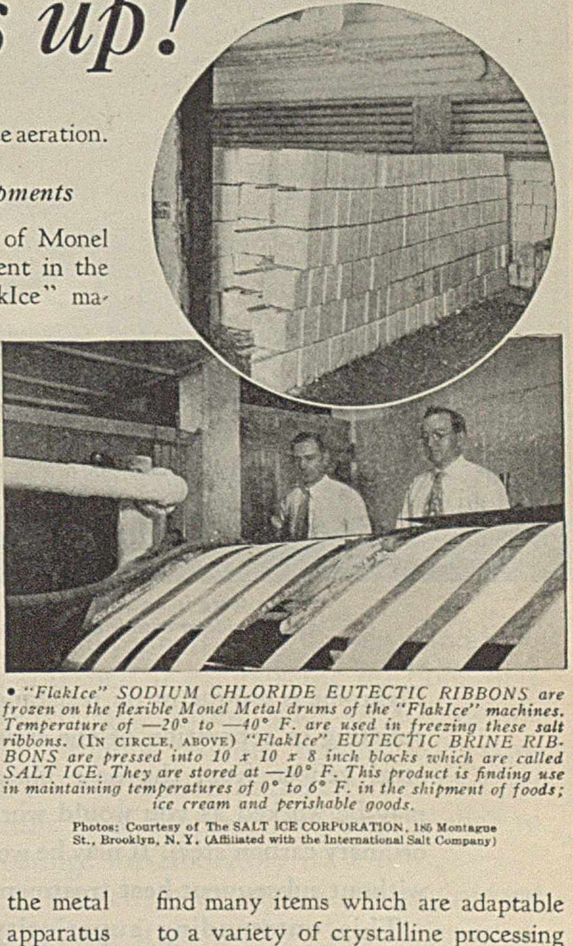
New and interesting uses of Monel Metal include its employment in the flexible cylinders of "FlakIce" machines for freezing sodium chloride brine ribbons; in rock salt dissolving tanks for the brine supplies of industrial and food product plants; and in salt washing chambers where crystals are washed in saturated brine solutions.

The enviable records made by Monel Metal in resisting corrosion by salt and brine explains its wide specification in installations where metal must be exposed to contact with sea water.

It is also of interest that the metal parts of salt spray testing apparatus subject to corrosion are almost invariably made of Monel Metal.

In the adjoining list of Monel Metal salt manufacturing equipment, you find many items which are adaptable to a variety of crystalline processing operations.

This equipment is available through leading fabricators. Consult them, or write us for further information.



• *"FlakIce" SODIUM CHLORIDE EUTECTIC RIBBONS are frozen on the flexible Monel Metal drums of the "FlakIce" machines. Temperature of —20° to —40° F. are used in freezing these salt ribbons.* (IN CIRCLE, ABOVE) *"FlakIce" EUTECTIC BRINE RIBBONS are pressed into 10 x 10 x 8 inch blocks which are called SALT ICE. They are stored at —10° F. This product is finding use in maintaining temperatures of 0° to 6° F. in the shipment of foods; ice cream and perishable goods.*

Photos: Courtesy of The SALT ICE CORPORATION, 185 Montague St., Brooklyn, N. Y. (Affiliated with the International Salt Company)

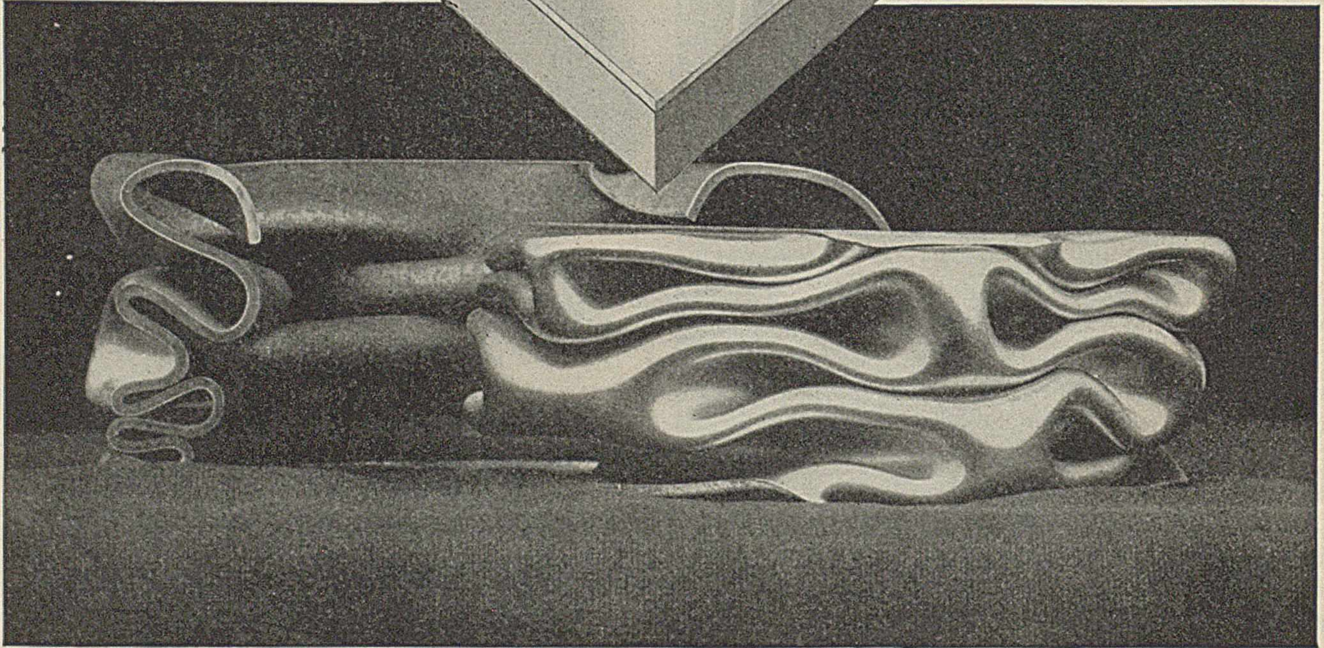
USES OF MONEL METAL IN SALT AND BRINE MANUFACTURE

- Baskets, centrifugal
- Bolts and Nuts
- Buckets
- Chutes
- Chains
- Conveyors, Screw
- Conveyors, Piping
- Dissolving Tanks
- Drain Boards
- Dryers, Rotary
- Expansion Joints
- Filters
- Filter Cloth
- Fittings
- Freezing Cylinders
- Grainer Aprons
- Grainer Rakes
- Hoppers
- Hydraulic Press Parts
- Linings & Flights
- Machinery, Packaging
- Nails and Screws
- Machinery, Weighing
- Parts, Machine
- Perforated Sheet
- Pump Rods
- Pump Valves
- Rivets
- Rotary Dryers
- Screening Equipment
- Shafting
- Sheet Metal Work
- Shovels
- Supply Tanks
- Tanks, Self-Supporting
- Tie Rods
- Tubing
- Utensils
- Valves
- Washing Tanks
- Wire Cloth
- Wire, Winding

THE INTERNATIONAL NICKEL COMPANY, INC.
67 WALL STREET NEW YORK, N. Y.

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.

Here's a Stainless Clad Plate that will take Punishment



Notice there is no separation of the stainless steel veneer from the backing plate in either inside or outside bends. You can work Plykrome without danger of fault or defect.

Plykrome is unique in its resistance to splitting or separation of the stainless steel veneer from the base plate. It may be worked as you would work an ordinary carbon steel. It may be welded without subsequent heat treatment.

This outstanding superiority of Plykrome is due to the use of a special metallic bond sheet between the stainless steel veneer and the base plate. The two metals are effectively bonded by an intermediary alloy formed by the bond sheet. Plykrome is the only stainless clad plate embodying this important principle of fabrication.

For many applications where corrosion resistance is required only on one side, Plykrome is practical, workable, and economical.

For detailed information on the application of Plykrome to corrosion resistance problems, consult our representatives.

USS

Illinois Steel Company

208 S. LA SALLE STREET, CHICAGO, ILLINOIS

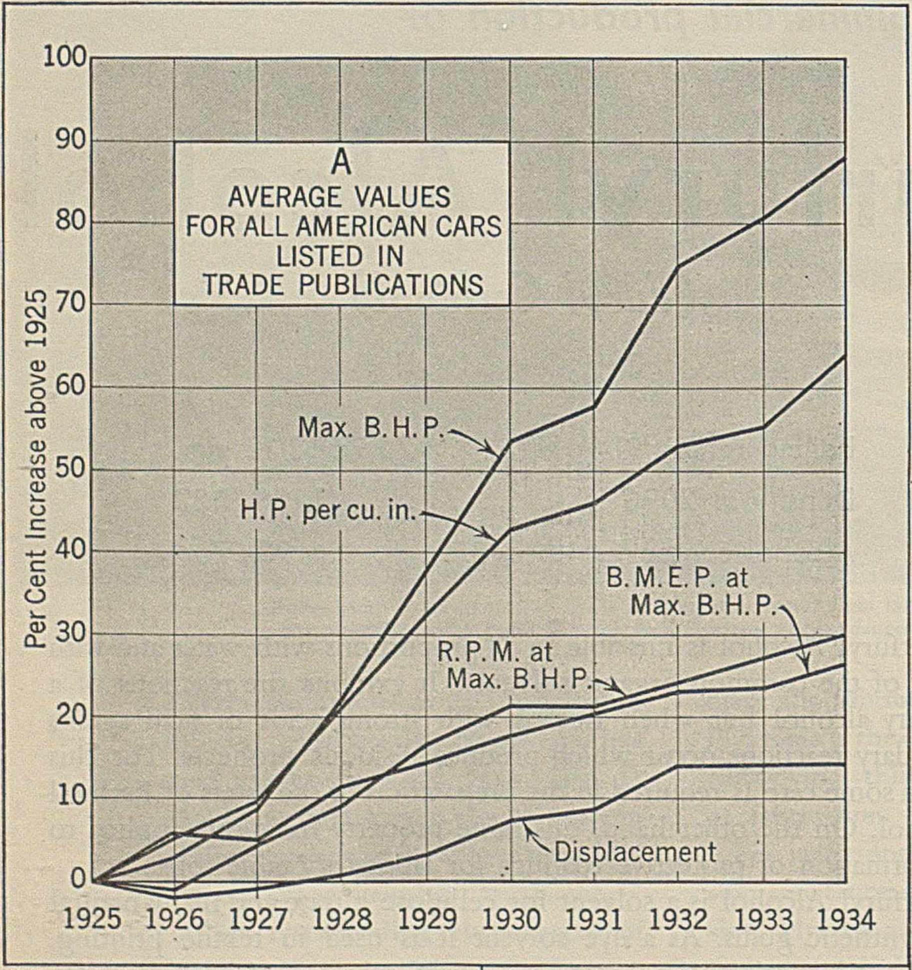
SUBSIDIARY OF UNITED STATES STEEL CORPORATION

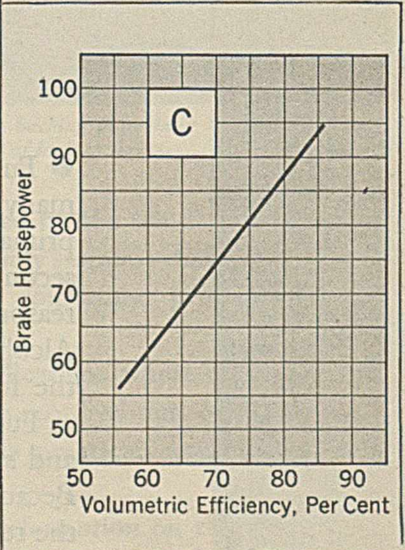
PLYKROME

USS CHROMIUM-NICKEL ALLOY STEELS ARE PRODUCED UNDER LICENSES OF THE CHEMICAL FOUNDATION, INC., NEW YORK, AND FRIED. KRUPP A. G. OF GERMANY

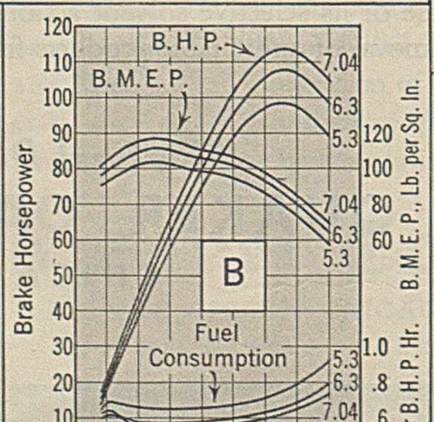
WHAT

in





A—Averages of all American cars listed in trade publications for annual change in five factors: (1) total displacement in cubic inches, (2) Brake mean effective pressure at maximum brake horsepower, (3) Revolutions per minute at maximum brake horsepower, (4) Horsepower per cubic inch of displacement, and (5) Maximum horsepower. Each of these factors is shown in percentage of gain over average value in 1925.



B—These curves show data that were obtained in tests of a typical eight-cylinder engine at three different compression ratios. Each increase in compression provides greater power and better fuel economy, and, although the data are not shown here, lower exhaust gas temperatures, decreased heat to cooling water, and lower extreme bearing loads also result.

C—The power gains to be expected from increases in volumetric efficiency are indicated by this curve. The data were taken in tests at constant speed on a large six-cylinder engine.

Ethyl Gasoline contains sufficient lead (tetraethyl) to make it the world's quality motor fuel.

are you going to do 1935?

TAKING shape on the drafting boards of power plant engineers are engines that will make obsolete the new wonders America is acclaiming today.

Some of these projected power plants will be born for success.

Because it is your intention to build one which will be successful, and because power increases will probably help toward that end, we print this resume:

Power history—what is it?

On the opposite page, chart "A" illustrates the steadily increasing horsepower of the average American car. It also points out the component factors which caused this general increase.

That is for the *average* car—all cars.

Who made the increases?

Ninety-four per cent of all cars sold in 1933 bore one of 12 nameplates, and their power history is even more pointed. Most of them showed horsepower gains for both 1933 and 1934, considerably greater than the averages indicated in chart "A."

Of the 21 different models made under the 12 names mentioned, 19 were more powerful in 1933 than they were in 1932, and 18 are more powerful in 1934 than in 1933. The average gain per model for the two years was 14.4 horsepower.

Apparently, people who buy automobiles like power and MORE power. Certainly, that idea seems to have occurred to the makers of these successful cars.

How were the power gains made?

In fundamental terms, there are only three ways to increase engine power. These factors may be expressed in simple algebraic form:

$$\text{Horsepower} = \frac{\text{B.M.E.P.} \times \text{Displacement} \times \text{R.P.M.}}{792{,}000}$$

Any increase in horsepower for *your* 1935 car will come from an increase in one or more factors in the numerator above.

Greater Displacement?

Bigger engines mean longer and heavier chassis, more difficult cooling problems, lower cyclic efficiency, consequently: increased gasoline consumption, and comparatively low performance gains in proportion to power gains.

More Revolutions per Minute?

More revolutions per minute produce desirable results; however, they involve penalties which become increasingly significant as higher speeds are reached. Even increases of comparatively small magnitude normally require changes in one or more of the following features: camshafts, bearings, ignition systems, pistons, piston rings, connecting rods, valves, valve springs, carburetion, manifolding, cooling and lubrication.

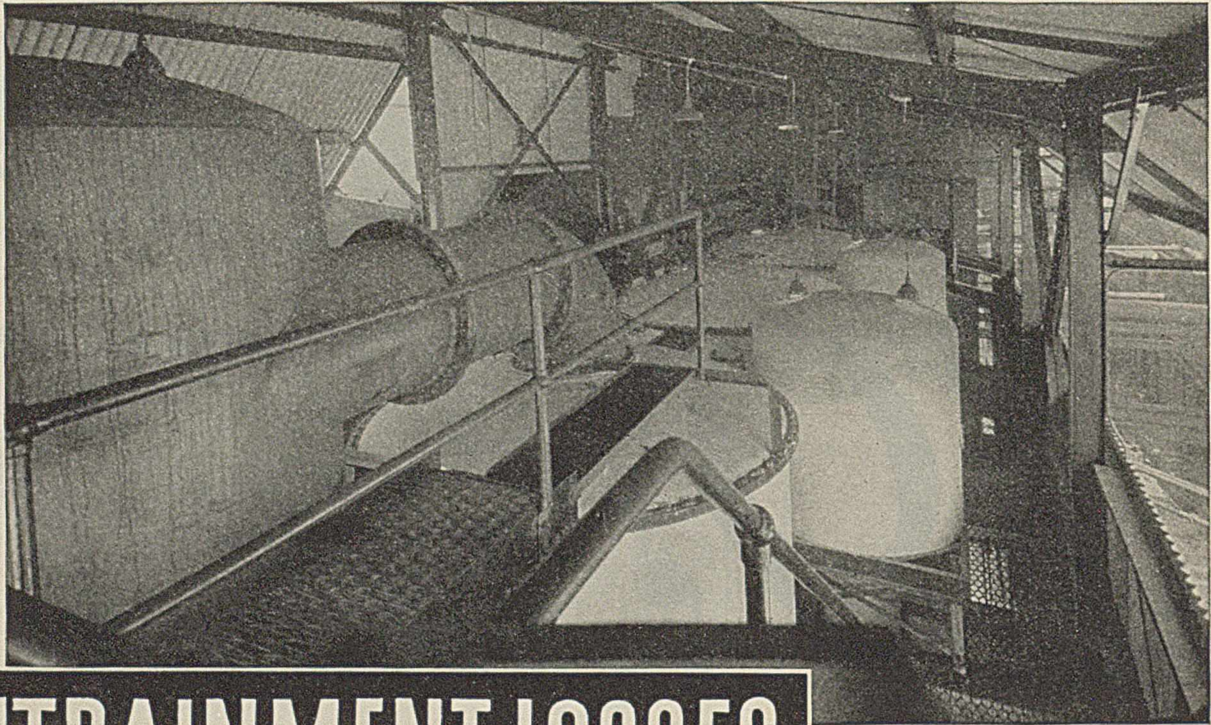
Higher B. M. E. P.?

Three out of four cars that have made power gains in the past two years got the added power, in whole or in part, through higher compression ratio. That is, of course, the easy, cost-less way to increase brake mean effective pressure. An example of the effects of increased compression on power and economy is shown in chart "B."

Another way of increasing brake mean effective pressure, which will be particularly helpful to those cars which already have the higher compression ratios, is improved volumetric efficiency. An example of the horsepower gains to be made in this manner is indicated in chart "C."

Fuel of sufficiently high anti-knock value to permit substantial increases in the brake mean effective pressures of most engines is available today in nearly every filling station in the United States and Canada.

Engineers of the Ethyl Gasoline Corporation will be glad to cooperate with you in any research or testing that may prove helpful in improving performance of your 1935 cars.



Industrial AND ENGINEERING Chemistry

Volume 26
Number 3

March
1934

Harrison E. Howe, Editor

The Editor's Page

SCIENCE SUFFERS BLOW. When President Roosevelt signed the Code of Fair Competition for the Graphic Arts Industries on February 17 science and education suffered the most severe blow of a decade. The problem of disseminating the results of scientific research in printed form became much more difficult because adherence to the provisions of this code will force upon the American Chemical Society and other scientific organizations an increase in cost estimated at 15 per cent as a minimum. Industrial and Engineering Chemistry, which rejected 35 per cent of the papers submitted in 1933, will find it necessary to enforce more rigidly its editorial policy in selecting for publication the reports of research conducted at great expense of time and treasure. Who can say which will be the most valuable data a generation hence? This new difficulty must presently confront authors as well as editors. Hence the following presentation of facts.

By far the greatest amount of printing done for scientific organizations is carried on in the smaller cities. Some of these establishments have grown with the coöperation of the societies concerned, not only in size and importance but in expert skill, and being located where overhead is obviously less than in metropolitan areas, they have been able to pay a wage scale satisfactory to employees and withal afford lower costs to the societies. The direct result has been a greater volume of scientific publication. It has been a mutually satisfactory arrangement in nearly every case. The smaller communities have been furnished with a dependable industry which has paid good wages and wide dissemination of scientific information has been made possible at a reasonable cost.

The situation, however, has been a thorn in the flesh of many metropolitan printers, who have preferred to stay in large cities, assume a much greater overhead, and pay the higher wages which are required for a scale of living often inferior to that possible in the less crowded centers at lower cost. The so-called country printer in his effort to expand has sought other orders and has been successful in obtaining them. The city printer has looked upon this as unfair competition and with the coming of the codes has decided to utilize this newest device to strengthen his position.

The original plan of the city printers was to have accepted as a part of the code a provision whereby charges would be based on the price prevalent at the point where the order was given, regardless of where the printing was to be done. That would have meant that manuscripts edited in any of the larger cities would be printed at prices prevailing there, even though the work might be done in a much smaller and distant community. As this involved building a tariff wall around a city, code authorities held it to be impossible and the plan was abandoned. In its place, however, another scheme was evolved. This imposed upon the small town printer a scale of wages and a provision as to apprentices which in effect forced his costs to the level existing in metropolitan centers. While hearings were being had on these several points, representatives of scientific societies called upon the Deputy Administrator, who then had the matter in hand for the National Recovery Administration, and were assured that if the wages of the plants in interest were restored, as requested by President Roosevelt, to the level of 1929 or, as a minimum, advanced 10 per cent beyond those in effect July 1, 1933, all would be well. However, these statements proved to be completely in error and provisions both as to rates of pay and apprentices formulated by a committee composed wholly of city printers was approved by the administration. The code as adopted exempts most of the printers of country newspapers, thereby reducing opposition to the new order.

The immediate effect of the code may be expected to spell a 30 per cent increase in labor costs in printing the Society's journals, or a net increase of 15 per cent in our publication expenses, since about half that cost is the class of labor indicated. Wage advances of this sort are commonly justified on the plea that the consumer is quite willing to pay an increased cost: first, because he is glad to help raise the plane of living; and second, because he will get some return from increased buying power. Neither of these applies to the publication of leading scientific periodicals. First, the plants in which these journals have been printed have been paying a scale generally higher than other crafts in areas which of themselves were centers of good wages. Second, scientific societies responsible for such publications cannot pass on increased costs to consumers, nor will they profit from these higher wages paid to workers. The direct result will be an increase rather than a decrease in unemployment. This is obvious when we remember that the societies have a definitely limited income with which they can purchase a certain volume of printing. When the price goes up, the volume must go down, and the ones who will directly lose are those supposed to be helped by the NRA type of legislation. The situation has been explained repeatedly to the highest authorities, but apparently the city has again won against the country. Some of those who have had to do with the code have seemed more interested in protecting the large investment of the city printer than in insuring continuance in business for his country competitor. It is a step in the direction of centralization and away from decentralization advocated by the chief executive. Under the circumstances there will be an enforced diminution in the volume of scientific research recorded. This is certain to retard industrial progress, which depends to an ever greater extent upon trends and developments in science. The blame, if any, for the results will not rest upon the scientific groups.

⁂

MIXED UNITS. Some years ago the Council of the AMERICAN CHEMICAL SOCIETY voted that thereafter authors reporting research and presenting data from laboratory procedures should in all cases express their results in metric units, though provision was made for the introduction of either metric or English equivalents, as the case might be, if for any reason that seemed preferable to the authors. The task of enforcing the Council rule has rested almost wholly with the office of INDUSTRIAL AND ENGINEERING CHEMISTRY.

There was much in favor of the action, for scientists, of all people, should be familiar with the metric system, especially having found it the most exact for their own uses. Furthermore, INDUSTRIAL AND ENGINEERING CHEMISTRY enjoys a world-wide circulation, and readers outside the English-speaking countries do their reading, thinking, and work in the metric system. However, the enforcement of the rule has involved no end of correspondence, has led to more than one discussion, and has made necessary extra time on the part of authors in recalculating tables of data and redrawing curves. Some of the difficulty has been with the data which are immediately useful in manufacturing establishments, provided only they are presented in the system in vogue in such factories, so that authors who themselves prefer the metric units have felt impelled to insist upon English measurements to further the utility of their work. Then, too, many testing machines are regularly graduated by the maker in the English system, and that leads to further work on the part of the investigator, if he would present his data in metric equivalents.

As a result of all this, we have taken it upon ourselves to apply the Council ruling with some discretion and decided not along ago that if a paper were consistent within itself, the exact adherence to the rule might be waived. However, it is most surprising to find the extent to which chemical engineers in particular mix their units of measurement. We strive for uniformity, but find the path almost as difficult as when we insisted on the metric system. Just why should an investigator who prefers degrees Centigrade feel satisfied when he mixes pounds per square inch or grains per gallon in the same table? We have even wrestled with results reported in grams or milligrams per ton, the exact nature of ton unrevealed, while cubic centimeters per gallon, likewise unidentified, are quite common. Really, any mixture of units, however absurd, seems possible and even formulas developed by chemical engineers can be found with both English and metric units freely admixed.

We appeal to our authors to save themselves and us, as well as our readers, from unnecessary work, not to say the jitters, by at least endeavoring to be consistent in the units of measurement employed in reporting their results. The irritation to be saved thereby will conserve nervous energy, which can be expended to far better advantage in the study of the paper and the assimilation of the truth it reveals.

⁂

EFFICIENCY. Some thought is being given in Washington to tariff programs, in which a point of far-reaching consequence has been raised. Would the United States profit by withdrawing tariff protection from inefficient industries? Presumably this would apply where, under our conditions, enterprises have not been developed to a place of importance in the national economy. So far no definitions have been offered, but with such points being given consideration in high places, industries may be doing themselves a good turn to learn from such reliable sources as qualified scientific opinion to what degree they are efficient. Data from such studies would serve to prove economic importance, and justification for reasonable tariff protection. Obviously all this involves problems of great complexity, going so far as population shifts, which might follow abandonment of certain industrial activities. Until some definite policy is announced discussion must be limited, but the present is a profitable time for industry to question itself to advantage and be prepared to meet such an issue if, and when, it is raised.

ANTIOXIDANTS ARE OF IMPORTANCE TO A WIDE VARIETY OF INDUSTRIES—IN FACT, WHEREVER VEGETABLE OILS AND FATS OR SIMILAR MATERIALS ARE EMPLOYED. ONE OF THESE USES IS IN THE MANUFACTURE OF PERFUMERY AND HERE IS SHOWN THE TREATMENT OF TUBEROSE BLOSSOMS BY THE PROCESS OF ENFLEURAGE. THE FLOWERS ARE PLACED IN FRAMES COATED ON THE INSIDE WITH FAT WHICH ABSORBS THE VOLATILE ESSENCE.

Photo by Lautier-Fils, Grasse

Antioxidants for Fats and Oils

GEORGE R. GREENBANK AND GEORGE E. HOLM

Bureau of Dairy Industry, Department of Agriculture, Washington, D. C.

INTENSIVE work on antioxidants began with the study by Moureu and Dufraisse (*6*) of the inhibiting effect of hydroquinone upon the oxidation of acrolein and of benzaldehyde. Their initial studies showed that substances having a phenolic group protected a number of autoxidizable compounds against the action of oxygen. Later work showed that various compounds, not necessarily phenolic in character, which under suitable conditions are easily oxidizable, act as antioxidants (*5*).

To explain the mechanism of antioxidants, these authors employ the theory of antagonistic peroxides. The principal steps therein may be illustrated as follows:

$$A + O_2 \longrightarrow A[O_2];\ A[O_2] + B \longrightarrow AO + BO$$
$$AO + BO \longrightarrow A + B + O_2$$

or

$$A + O_2 \longrightarrow A[O_2];\ B + O_2 \longrightarrow B[O_2]$$
$$A[O_2] + B[O_2] \longrightarrow A + B + 2O_2$$

where A = an activated molecule
B = the antioxidant

The antioxidative effect of phenol, alcohols, and other compounds upon fats and oils has been noted in a former publication from these laboratories (*3*). The present investigations deal with a further attempt to determine what other types of compounds may be effective as antioxidants for fats and oils.

EXPERIMENTAL METHOD

During the oxidation of fats and oils, peroxides are formed, their rate of formation being a measure of the ease with which an oil will oxidize. The amount of peroxide formed in a definite period of time under specified conditions serves, therefore, as an index of oxidation.

Untreated samples and samples to which 0.01 per cent of the antioxidant had been added were stored at a temperature of 42° C. for 10 days, and the peroxide content was then determined as follows: 50 cc. of a solution consisting of two parts of acetic acid and one part of trichloromethane by volume was added to a weighed sample of fat. To this mixture was added one cc. of a saturated aqueous solution of potassium iodide. The mixture was kept in the dark for 3 minutes, and 50 cc. of distilled water were then added. The liberated iodine was titrated with 0.002 N sodium thiosulfate. The number of cubic centimeters of 0.002 N sodium thiosulfate used per gram of fat is equivalent to the number of millimoles of peroxide per kg. of fat. The weight of the sample of fat used must be governed by the peroxide content. In no case should the iodine liberated be equivalent to more than 15 cc. of 0.002 N sodium thiosulfate. From 0.25 to 0.75 gram is usually a convenient and satisfactory quantity to use.

The results obtained have been expressed in terms of the relative amounts of peroxide formed in a sample of fat and in another sample of the same fat to which an antioxidant had been added. This has been designated as the protective factor (P. F.) and is obtained as follows:

$$\text{P. F.} = \frac{\text{millimoles of peroxide per kilogram of untreated fat}}{\text{millimoles of peroxide per kilogram of treated fat}}$$

A protective factor of 1.0 indicates, therefore, no protective action.

NATURAL PIGMENTS

Certain oils, especially those of plant origin, contain carotinoid pigments. These pigments are also constituents of some animal fats and oils, especially butter fat. That these pigments influence the rate of fat oxidation has been shown by Olcovich and Mattill (*8*) who maintain that carotene is a procatalyst. Monahan and Schmitt (*4*), as well as Newton and Richardson (*7*), class this compound as an antioxidant. The results of Franke (*1*) agree in general with those of Olcovich and Mattill. Franke found that carotene and lycopene were antioxidants for acids but not for their glycerides.

To ascertain the extent to which natural coloring matter might be a factor in determining the rate of peroxide formation, the effect of the lipochromes carotene and lycopene, and a flavone, quercetin, when added to a fat has been determined. The results are given in Table I.

TABLE I. NATURAL PIGMENTS AS ANTIOXIDANTS IN COTTONSEED OIL

	PEROXIDES IN:		
	Untreated sample	Treated sample	P. F.
	Millimoles per kilogram		
Carotene	25.0	27.1	...
Lycopene	25.0	24.9	1.0
Quercetin	25.0	13.2	1.9

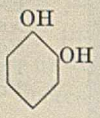
The results with carotene agree with those of Franke, which showed that lipochromes accelerate oxidation of glycerides. Quercetin, on the other hand, seems to possess antioxidative properties.

PHENOLS

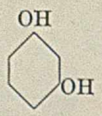
Hydroquinone has been used extensively in the study of antioxidative action, but no systematic study of the action of its related compounds on fats and oils has been made, although Moureu and Dufraisse (*6*) found in their initial studies that hydroquinone, pyrocatechol, and pyrogallol possessed far greater antioxidative properties than did phenol and resorcinol.

The relative values of hydroquinone, catechol, and resorcinol as antioxidants were first determined:

Hydroquinone
P. F. = 3.7

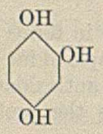


Catechol
P. F. = 2.0

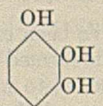


Resorcinol
P. F. = 1.1

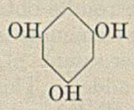
These results are, in general, analogous to those obtained by Moureu and Dufraisse in that 1.2- and 1.4-dihydric phenols give protection against oxidation of oils but 1.3-dihydric phenol offers little protection. It seems probable that the explanation may lie in the fact that the 1.2- and 1.4- compounds form quinones and are, therefore, capable of forming oxidation-reduction systems. The trihydric phenols—hydroxyhydroquinone, pyrogallol, and phloroglucinol—were also tried as antioxidants with the following results:



Hydroxyhydroquinone
P. F. = 3.6



Pyrogallol
P. F. = 3.6



Phloroglucinol
P. F. = 1.0

In this experiment phloroglucinol, analogous in structure to resorcinol, failed to show antioxidative properties.

OTHER AROMATIC COMPOUNDS

Table II shows the protective action of hydroquinone and closely related compounds. The protective action of the acids, especially that of phthalic acid, is of unusual interest, as will be shown later.

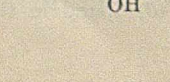
TABLE II. AROMATIC COMPOUNDS AS ANTIOXIDANTS IN COTTONSEED OIL

	Peroxides in: Untreated sample	Treated sample	P. F.
	Millimoles per kilogram		
Hydroquinone	25.6	6.9	3.7
Phenol	29.4	29.6	1.0
Benzaldehyde	29.4	38.4	...
Phthalic acid	25.6	8.1	3.0
Cinnamic acid	31.7	25.7	1.2
Anthranilic acid	20.0	14.1	1.4

ALIPHATIC ACIDS

The excellent keeping quality of raw vegetable oils is thought to be due to the natural antioxidants that are present in the raw oil but are destroyed or removed in the refining processes. An unsuccessful attempt was made to isolate an antioxidant from cottonseed. Of the various extracts prepared, only the water-soluble less the heat-coagulable protein fraction showed protective qualities. This extract was slightly acidic, and results with it in addition to the results already obtained with acids formed the basis for a further study of the antioxidative action of various organic acids.

In the choice of acids to study in this connection, the authors were guided somewhat by the assumption that protective action is in some way related to the structures:

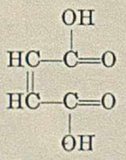


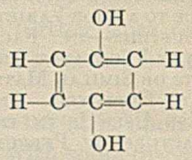
$$-\overset{H}{C}=\overset{H}{C}-\underset{OH}{C}=O$$

or

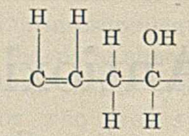
$$-\underset{H}{C}=\underset{H}{C}-\underset{H}{C}(OH)-$$

The similarity between the structure of maleic acid, which proved to be a good antioxidant, and that of hydroquinone is indicated in the following formulas:





Former work with ricinoleic acid (3) had indicated that a hydroxy group on carbon atoms farther removed from the double bond is also effective in preventing autoxidation. This grouping in ricinoleic acid is considered to be as follows:



Maleic, fumaric, aconitic, and other acids were therefore studied with respect to their properties as antioxidants. The results obtained are given in Table III.

TABLE III. ACIDS AS ANTIOXIDANTS IN COTTONSEED OIL

Acid	Peroxides in: Untreated sample	Treated sample	P. F.
	Millimoles per kilogram		
Maleic	25.6	8.2	3.0
Malic	18.0	13.5	1.3
Citraconic	25.6	12.8	2.0
Itaconic	25.6	13.4	1.9
Aconitic	25.6	16.0	1.6
Succinic	28.6	22.5	1.3
Tartaric	25.2	21.2	1.2
Citric	25.6	14.2	1.8
Crotonic	25.1	49.0	...
Fumaric	20.0	15.3	1.3

As indicated, maleic acid was the most potent antioxidant of those tried. It is a surprising, as well as an important, fact from the standpoint of an explanation of the mechanism of action of antioxidants, that fumaric acid, the isomer of maleic acid, does not act as an antioxidant. The efficiency of maleic acid as an antioxidant when added to various fats that differ in their constituency of unsaturated fatty acids was determined in a manner similar to that already described. In each case the concentration of maleic acid in the treated sample was approximately 0.01 per cent, and the treated and untreated samples were stored at 42° C. for 10 days. The results are shown in Table IV.

TABLE IV. MALEIC ACID AS AN ANTIOXIDANT IN DIFFERENT OILS

Oil	Peroxides in: Untreated sample[a]	Treated sample[a, b]	P. F.	Rancidity Appeared: Untreated sample[a]	Treated sample[a, b]
	Millimoles per kg.			*Days*	*Days*
Butter	3.2	1.2	3.5	15	47
Cottonseed	25.6	8.2	3.1	10	28
Corn	60.9	11.5	5.3	15	65
Sunflower	27.2	8.2	3.3	12	38
Peanut	25.7	8.1	3.1	13	37
Cod liver	26.7	8.2	3.2	..	..
Lard	15.1	5.0	3.0	13	36
Linseed	40.0	13.3	3.0	..	..
Oleic acid	20.0	6.5	3.0	..	..

[a] Stored 10 days at 42° C.
[b] Contained 0.01 per cent of maleic acid.

For every fat except corn oil the protective factor with maleic acid was approximately 3.0. For corn oil a P. F. of 5.3 was obtained, probably because of the fact that this oil does not normally oxidize as readily as do the other oils tried.

With each fat the fact was noted that greater protective action was always obtained with an antioxidant when fresh samples of good keeping quality are used. In other words, the protective factor increases with improved keeping quality of the oils.

Throughout the experiments it was also noted that in the presence of traces of water the acids are not so effective as antioxidants as they are in dry oils. It was thought that compounds of maleic acid that are more soluble in fats, such as the salt, anhydride, or ester, would lend themselves better to a quantitative study of the antioxidant than did maleic acid. However, when these were tried, none of the compounds showed antioxidant properties except the anhydride, which may owe this action to a reversion of a small amount to the acid form.

SUMMARY

Of the phenols, only the ortho and para types are active as antioxidants for fats and oils. Some unsaturated polybasic aliphatic acids (*2*), notably maleic, are also antioxidants for fats and oils.

LITERATURE CITED

(1) Franke, W., *Z. physiol. Chem.*, **212**, 234 (1932).
(2) Greenbank, G. R., U. S. Patent 1,898,363 (Feb. 21, 1933).
(3) Holm, G. E., Greenbank, G. R., and Deysher, E. F., IND. ENG. CHEM., **19**, 156 (1927).
(4) Monahan, B. R., and Schmitt, F. O., *J. Biol. Chem.*, **96**, 387 (1932).
(5) Moureu, C., and Dufraisse, C., *Chem. Rev.*, 3 (2), 113 (1926).
(6) Moureu, C., and Dufraisse, C., *Compt. rend.*, 174, 258 (1922).
(7) Newton, R. C., *Oil & Soap*, p. 247 (Nov., 1932).
(8) Olcovich, H. S., and Mattill, H. A., *J. Biol. Chem.*, **91**, 105 (1931).

RECEIVED September 27, 1933.

Photochemical Studies of Rancidity

Peroxide Values of Oils as Affected by Selective Light

MAYNE R. COE AND J. A. LECLERC, Bureau of Chemistry and Soils, Washington, D. C.

THE decomposition products of oils have heretofore been used as indices of the degree of rancidity. The presence of these split products has been indicated by the well-known Kreis test (*8*), the modified Schiff's test, sometimes called the von Fellenberg test (*3*), and certain other color tests. The peroxide value of oils likewise has been used as a measure of the degree of rancidity.

Heffter (*5*), Taffel and Revis (*12*), Lea (*9*), and more recently Wheeler (*13*), Royce (*11*), Kilgore (*6*), and King, Roschen, and Irwin (*7*) have studied the oil from this viewpoint.

Certain investigators have shown that occasionally an oil, known to be freshly made, will give a positive reaction for rancidity with these various color tests. For instance, Powick (*10*) concludes: "A positive reaction in the Kreis test when the test is performed in the usual manner, is not always a reliable indication of rancidity in fats. A large number of compounds react with phloroglucinol-hydrochloric acid to give a red color that, to the unaided eye, is indistinguishable from the color obtained with rancid fats."

Recently Greenbank and Holm (*4*) studied with the use of the Mazda lamp the photochemical oxidation of cottonseed oil as measured by the reduction of methylene blue and arrived at the conclusion that blue light was the least effective in accelerating oxidation as compared to green, red, or amber of the same light energy.

Davidsohn (*2*), in a discussion on the rancidity of fats and oils, gives the conclusion of the German Fat Analysis Commission, which declares that taste and odor are so far the only reliable tests for rancidity. It is generally admitted, however, that, when an oil is found to be rancid by these organoleptic tests, it will also give a positive Kreis or von Fellenberg reaction.

Wheeler, in a modification of Lea's method, bubbled moist air through corn oil or cottonseed oil maintained at 100° C. in an enclosed compartment which happened to be lightproof, and found that peroxide values of the oil mounted to a certain point at which the oil became rancid. The peroxide value, however, continued to increase for a time but finally decreased. A curve was plotted showing the point at which, under the conditions of the experiment, an oil would become rancid. The entire curve up to that point could be considered as the measure of the induction period, or the period during which the oil remained free from rancidity.

The present investigation is primarily concerned with the photochemical effect of light on the development of peroxides as a measure of rancidity in oils, the purpose being to determine the trend of peroxide formation in oils kept at room temperature and protected from all light, and also in oils protected by green light delimited by 4900 to 5800 Å.

RANCIDITY TESTS ON OILS

CORN OIL. This oil, which in previous experiments (*1*) had been used for frying potato chips, was divided into two portions. One was protected from light by wrapping with opaque black paper and the other was wrapped with unglazed white manifold paper. Both portions were placed in a south window for exposure to direct sunlight. The same was also done with a portion of the original unused oil. The peroxide values were determined at the beginning and approximately at each week throughout the experiment. Table I gives the results.

TABLE I. PEROXIDE VALUES OF CORN OIL

DATE	ORIGINAL OIL BEFORE USE		USED OIL	
	Black	Clear	Black	Clear
4/15/32	8.4	8.4	8.8	8.8
4/22/32	17.7	49.5	15.2	30.7
5/3/32	28.8	73.9 R[a]	20.5	44.2 R
5/9/32	31.5	111.5 R	28.0	61.2 R
5/17/32	36.3	207.6 VR	32.1	81.2 R
5/26/32	44.2	205.6 VR	40.1	105.5 VR
6/3/32	49.6	240.3 VR	44.1	137.5 VR
6/10/32	54.4	269.5 VR	50.3	198.9 VR
6/17/32	65.1	340.0 VR	62.0	206.9 VR
7/11/32	99.1	489.2 VR	79.1	306.6 VR
7/25/32	117.2	616.0 VR	100.0	508.5 VR

[a] R = rancid; VR = very rancid.

Peroxide values increased rapidly in the sample unprotected from light, and the oil wrapped with black paper remained free from organoleptic rancidity to the end of the experiment, even though it had at that time developed a peroxide value much above that of the unprotected oil at the time rancidity was first recorded (Figure 1). During the time of the experiment there was no decrease in the peroxide value such as was noted by Wheeler (*13*) in his experiments carried on at 100° C.

CORN OIL BUBBLED WITH AIR. In another experiment, air was bubbled through bottled samples of corn oil at the rate of 6 liters per hour, with the samples protected from light as follows: One bottle was wrapped with opaque black paper, one with green transparent cellulose adjusted to cut out most of the blue wave lengths, one with clear transparent cellulose; the fourth, or control, was not wrapped. These samples were exposed to the diffused light of the laboratory and the peroxide values were determined at approximately weekly intervals until the oil in the clear bottles became so viscous that air could no longer bubble through it. The experiment covered a period of more than 7 months; the results are recorded in part in Table II.

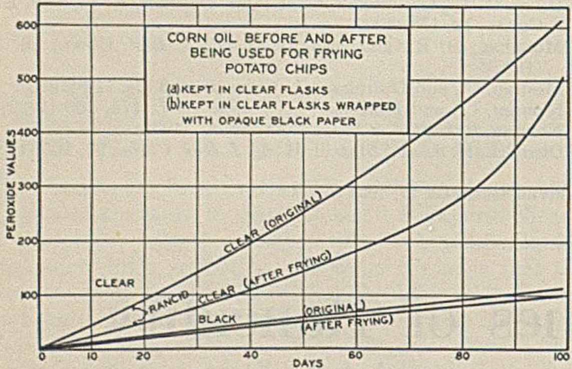


FIGURE 1

TABLE II. PEROXIDE VALUES OF CORN OIL BUBBLED WITH AIR, PROTECTED AND UNPROTECTED FROM LIGHT

Date	Original Tin Container[a]	Test Bottles (Clear Glass): Color of Wrapping: Black	Green	Clear	Not wrapped
8/26/32	4.9	4.9	4.9	4.9	4.9
8/27/32	8.0	9.4	11.0	12.1	12.9
9/12/32	22.1	23.9	24.7	34.3	38.0
9/26/32	31.0	33.7	36.8	48.5	54.6
10/3/32	36.4	39.5	42.0	54.8 R[b]	66.4 R
10/17/32	41.3	43.1	46.6	59.2 R	73.3 R
11/7/32	50.2	52.0	46.6	72.5 R	87.1 R
11/2/32	61.5	55.8	64.7	81.4 R	94.1 R
12/5/32	68.3	70.0	71.5	93.5 R	114.7 VR
12/19/32	77.9	73.0	79.0	106.9 VR	130.0 VR
1/10/32	87.1	78.0	88.3	135.4 VR	197.0 VR
1/17/33	92.0	82.3	91.3	146.5 VR	274.3 VR
1/31/33	96.6	85.7	98.3	180.9 VR	828.0 VR
2/7/33	101.5	91.6	101.0	212.5 VR	950.5 VR
2/14/33	98.3	84.6	96.8	330.5 VR	Too viscous
2/21/33	100.3	89.8	99.7	609.9 VR	...
2/28/33	111.1	95.5	108.7	893.7 VR	...
4/11/33	134.8	116.4	138.5	Too viscous	...

[a] Not blown with air.
[b] R = rancid, VR = very rancid.

The results show that the oil in the original tin container and that protected by black or green wrappers remained free from rancidity throughout the experiment.

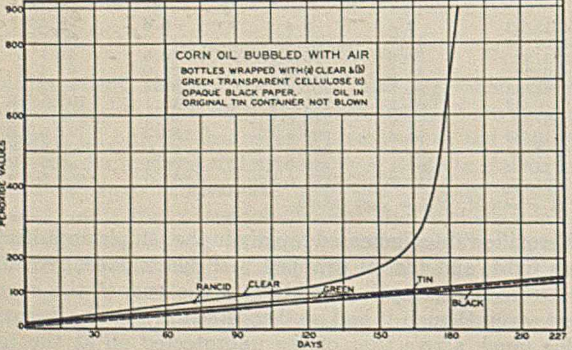


FIGURE 2

The peroxide values of the oils in the clear bottles increased gradually up to approximately 200, and at the same time the color was gradually bleached. In the three succeeding weeks the peroxide value jumped to over 800, and by that time the oils had become not only fully bleached but very viscous (Figure 2). The characteristic rancid odor was strong. A drop or two of the viscous oil that was spread on a block of wood solidified and dried just as does linseed oil. The oils that were protected from light remained limpid and retained their natural color far beyond the duration of the experiment.

COTTONSEED OIL. A third experiment using cottonseed oil was set up as follows: A portion of the oil was placed in each of four glass flasks: (1) a green flask transmitting light of wave lengths between 4900 to 5800 Å.; (2) a clear Pyrex glass flask covered with green paper of similar light transmission; (3) a blue flask which transmitted violet, blue, and some green; (4) a clear Pyrex glass flask which allowed all visible wave lengths of light to be transmitted almost unrestrictedly (Figure 3). Air was bubbled through the oil in each of these flasks at the rate of 6 liters an hour. Peroxide values were determined weekly.

Table III shows a comparison of peroxide values when air was passed through cottonseed oil contained in green, blue, and clear flasks, and exposed to diffused light of the laboratory.

It is significant that the oil in the green flask (1) and that in the clear flask (4) had practically the same peroxide value at the end of the experiment, yet the former was free from rancidity while the latter was appreciably rancid. The oil in the blue flask (3) had an even higher peroxide value than that in the clear flask at every stage of the experiment (Figures 4 and 5). It also became rancid at an early stage.

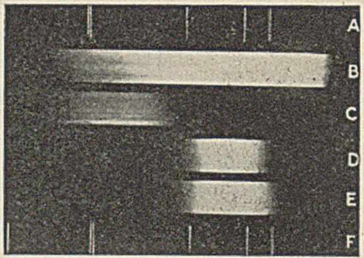


FIGURE 3. SPECTRA OF PROTECTIVE AND NONPROTECTIVE FLASKS

A, *F*. Spectrum lines of mercury arc
B. Spectrum of Mazda light source
C. Transmission of blue flask
D. Transmission of green flask
E. Transmission of flask covered with green paper

TABLE III. PEROXIDE VALUES OF COTTONSEED OIL BUBBLED WITH AIR, PROTECTED AND UNPROTECTED FROM LIGHT

Date	Flask: 1	2	3	4
4/26/33	14.8	14.8	14.8	14.8
5/9/33	18.1	14.4	21.1	20.0
5/16/33	26.8	19.6	34.9	30.3
5/23/33	42.8	30.7	54.0	47.9
6/6/33	71.2	48.2	85.9 R[a]	76.5 R
6/13/33	93.5	63.3	108.8 R	95.00 R
6/20/33	95.1	65.5	114.5 R	100.9 R
6/27/33	111.0	78.4	126.4 R	114.1 R

[a] R = rancid.

There are numerous references in the literature which show that the development of rancidity is a process of oxidation—i. e., the result of the addition of molecular oxygen to the unsaturated double bond. If this is true, it might follow that an oil could be stabilized against rancidity by bubbling air through it in a black or green container. Therefore, the sample of corn oil which had been protected in a black bottle during aëration and which had developed a peroxide value of 116.4 (Table II) was divided into two portions; one portion (1) was placed in a test tube protected with the special green paper and the other (2) in an unprotected clear test tube. Both were exposed to the light of an east window for 52 days. In sample 1 the peroxide value increased to 197, but no rancid odor or taste developed. In sample 2 the peroxide value increased to 210, and the oil smelled and tasted rancid. These results show that molecular oxygen introduced by bubbling air through the oil protected from light did not produce a stable oil. It should be noted that the peroxide value of the portion protected by green is fully three times as high as the value given in Table II, columns 5 and 6, where rancidity was first noted. This experiment seems to furnish evidence that organoleptic rancidity may not be due solely to the formation of peroxides as has been believed, but possibly to an independent compound whose formation accompanies the development of peroxides.

Further evidence that the compound giving rise to the rancid odor and taste is not developed when the oil is protected from light is shown in Figure 6, which gives spectra of the light transmitted by the corn oil whose peroxide values are recorded in Table II. The first exposure represents spectrum lines of a mercury lamp in order to establish the position of the various wave lengths of light; the second is the spectrum of the Mazda light source; the third is of Mazda light transmitted by 2 cm. of rancid corn oil (peroxide value approximately 900); the fourth is that of Mazda light transmitted by 2 cm. of corn oil which had been protected from light (peroxide value 116.4, but not rancid); the fifth is that of a different corn oil, not rancid, with a peroxide value 3.8.

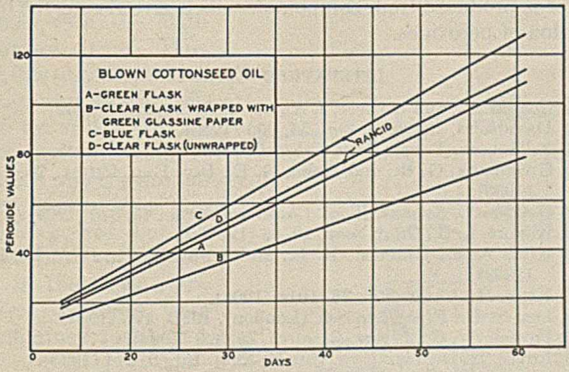


FIGURE 4

The spectra of the light source and of the rancid oil are almost identical, indicating negligible absorption of light by the oil; those for the protected oil and the oil of low peroxide value are similar to each other and indicate strong absorption of blue light. Disappearance of ability to absorb blue light apparently is accompanied by development of rancidity (*9*). This is being studied at the present time.

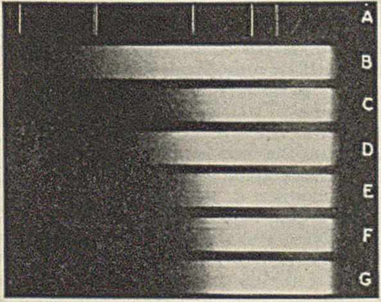


FIGURE 5. SPECTRA OF COTTONSEED OIL SAMPLES

A. Spectrum lines of mercury arc
B. Spectrum of Mazda light source
C. Transmission of rancid oil from clear flask
D. Transmission of rancid oil from blue flask
E. Transmission of nonrancid oil from green flask
F. Transmission of nonrancid oil from flask covered by green paper
G. Transmission of fresh oil (not aërated)

DISCUSSION OF RESULTS

The Kreis and similar color tests have heretofore been employed as a means of detecting rancidity in oils. The peroxide value of an oil as a measure of incipient rancidity has recently been suggested as a substitute for the Kreis and von Fellenberg color tests. Photochemical action in the development of rancidity has heretofore been given but little attention.

In a recent paper by the present authors (*1*) it was shown that green light (delimited by 4900 to 5600 Å.) delayed the appearance or the development of rancidity almost to the same extent as does the exclusion of all light. There is no doubt that oxidation takes place continually in oils and fats, but this action, as measured by the peroxide values, proceeds more rapidly in the presence of light than when all light is excluded. Furthermore this oxidation process, in the presence of light, is accompanied by the development of organoleptic rancidity; hence the formation of the compound giving rise to organoleptic rancidity may be credited chiefly to the effect of light.

In the present experiments the peroxide value of oils, kept at room temperature, did not decrease after reaching a certain point. On the contrary, the values increased gradually to about 200 and then increased rapidly until about 800 was reached, at which point the oil began to solidify. The oils protected by black, or by green of the proper light transmission, showed a relatively slow increase in peroxide value throughout the experiments, remained limpid, and retained more nearly their original color for more than 7 months. The unprotected oils used in these experiments became rancid at room temperature when the peroxide value was in the neighborhood of 60, which is about twice the value found by Wheeler whose oils were kept at 100° C.

The present experiments show that oxidation goes on as fast in blue light as in clear light, and much faster than in green light. Green light furnished by the filter used is to a large degree photochemically inert in the development of rancidity because it absorbs the light included in the blue and red ends of the spectrum. In no case were the protected oils organoleptically rancid, although they gave the characteristic color reaction with the Kreis and von Fellenberg reagents. This reaction is frequently obtained with freshly made cottonseed oil.

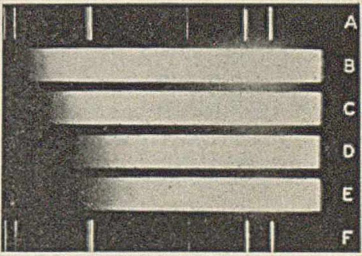


FIGURE 6. SPECTRA OF OIL SAMPLES PROTECTED FROM LIGHT

A, F. Spectrum lines of mercury arc
B. Spectrum of Mazda light source
C. Transmission of rancid oil
D. Transmission of nonrancid oil
E. Transmission of fresh oil (not aërated)

A strong indication that oxidative rancidity is due principally to the effect of light and not entirely to the formation of peroxides is shown by the present results. The protected oil which had previously developed a high peroxide value, without, however, showing signs of organoleptic rancidity, became rancid after exposure to light. This observation is significant because it furnishes evidence that the compound giving rise to the rancid state is the result of photochemical action due to absorption of light possibly by a compound already present in the oil. The formation of peroxides may be accelerated by the presence of light, but the process which gives rise to rancidity appears to be independent of, or accompanies the formation of peroxides. The composite results from the experiments here reported, in which the oil was protected from light, seem to invalidate the chemical tests heretofore used for the detection of rancidity or incipient rancidity of an oil, and apparently support the view that organoleptic tests are the only reliable tests for rancidity, regardless of whether or not an oil has been exposed to light.

Additional evidence that the compound which gives rise to the rancid state is independent of or accompanies the formation of peroxides is shown by the spectra of Figure 6. Both the protected oil and the fresh oil have absorbed to a large extent the blue end of the spectrum. The rancid oil has, because of exposure to light, undergone photochemical change to such an extent that its spectrum is nearly the same as for the light source alone. The fact that the spectrum for the nonrancid oil with a peroxide value of 116.4 corresponds almost identically with that for the fresh oil with a peroxide value of 3.8 further supports the view that oxidative rancidity is due apparently to photochemical action of light on a compound which probably exists simultaneously with or is produced from the compounds which give rise to the formation of peroxides.

SUMMARY

1. The well-known color tests for rancidity and the peroxide test for the decomposition of an oil may not show conclusively that an oil is rancid. These tests are not reliable when applied to oils which have been properly protected from light.

2. Oils which have been protected from light with opaque black paper, or with green paper transmitting light delimited by 4900 to 5800 Å., remain free from rancidity even though they may have a peroxide value equal to or higher than an unprotected oil which has become rancid.

3. Similar results have been obtained when air has been bubbled through the oils at the rate of 6 liters per hour.

4. Oils protected from light as described have not shown any organoleptic rancidity even after a period of 7 months, although they gave strong positive tests with both the Kreis and the von Fellenberg reagents, and also showed relatively high peroxide values.

5. A portion of a protected sample of oil still free from organoleptic rancidity but having a peroxide value higher than that of an unprotected rancid oil was exposed to diffused daylight. By the end of 52 days it had acquired a rancid odor and taste, while the original protected portion of the same sample remained free from rancidity.

6. In the case of cottonseed oil and corn oil the results of these experiments support the view that oxidative rancidity may be due principally to photochemical action of light on a compound which probably exists simultaneously in the oil or is produced from compounds which give rise to the formation of peroxides.

LITERATURE CITED

(1) Coe, M. R., and LeClerc, J. A., *Cereal Chem.*, 9, 59 (1932).
(2) Davidsohn, I., *Chem.-Ztg.*, 54, 606 (1930).
(3) Fellenberg, T. von, *Mitt. Lebensm. Hyg.*, 15, 198 (1924).
(4) Greenbank, G. R., and Holm, G. E., IND. ENG. CHEM., 25, 167 (1933).
(5) Heffter, A., *Schweiz. Woch. Chem. u. Pharm.*, 42, 320 (1904).
(6) Kilgore, L. B., *Oil & Soap*, 10, 66 (1933).
(7) King, A. E., Roschen, H. L., and Irwin, W. H., *Ibid.*, 10, 105 (1933).
(8) Kreis, H., *Chem.-Ztg.*, 26, 1014 (1902).
(9) Lea, C. H., *Proc. Roy. Soc.* (London), 108B, 175 (1931).
(10) Powick, W. C., *J. Agr. Research*, 26, 323 (1923).
(11) Royce, H. D., IND. ENG. CHEM., Anal. Ed., 5, 244 (1933).
(12) Taffel, A., and Revis, C., *J. Soc. Chem. Ind.*, 50, 87T (1931).
(13) Wheeler, D. H., *J. Oil & Soap*, 9, 89 (1932).

RECEIVED September 26, 1933. Presented before the Division of Agricultural and Food Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933. This paper is Contribution 197 of the Food Research Division, Bureau of Chemistry and Soils.

Heat Requirements for Fatty Acid Distillation

VICTOR MILLS AND R. C. DANIELS, The Procter & Gamble Company, Ivorydale, Ohio

WITH the old bottom-fired type of fatty acid still commonly used in the oil and fat industry until recently, there was little need for accurate data on heat requirement. With the advent of stills heated with steam or hot water, the need of dependable figures for latent heat of vaporization of fatty acids became more apparent.

A number of writers have reported theoretical values for latent heat of pure fatty acids. All of these values are calculated directly or indirectly from vapor pressures by use of the Clausius-Clapeyron equation. The only experimental data of a technical nature seem to be those obtained in 1920 by Alsberg (*1*). Alsberg obtained values of 118 and 130 B. t. u. per pound (65.5 and 72.2 calories per gram) on two different runs of cottonseed fatty acids. A careful perusal of his method, however, leaves considerable question as to the accuracy of the results. There are far too many assumptions and estimates involved.

The writers recently had occasion to determine the steam usage in the heating coils of a Gensecke type of fatty acid still. Data were obtained from which a more dependable value for the latent heat of vaporization could be calculated.

EQUIPMENT AND MODE OF OPERATION

The still illustrated in Figure 1 is a standard make manufactured by the Lurgi Gesellschaft für Wärmetechnik and covered by Gensecke's patents (*2*).

The heating element in the still, *a*, consists of two copper coils of approximately 270 square feet (25 square meters) mean surface. Steam at about 450 pounds per square inch (32 kg. per sq. cm.) gage pressure is supplied by a motor-driven compressor, *b*. Vacuum is maintained at 7 to 10 mm. of mercury by use of steam ejectors, *c*. Approximately 10,000 pounds (4536 kg.) of crude fatty acid are charged to the still at the start of a run, and thereafter for about 20 hours the feed is continuous to maintain an even level. The crude stock going to the still is preheated by passing through a heat exchanger, *d*, which also serves as a partial condenser for the fatty acid vapors. Most of the distillate is condensed in the jacketed coolers, *e*. A small amount of stock is condensed and baffled out in separator *f* and measured in receiver *g*. The bulk of the distillate is received in *h* and pumped out, under vacuum, to storage.

HEAT MEASUREMENTS

Measurement of the heat used for distillation was accomplished by weighing the steam condensate from the heating coils. In order to avoid loss of water due to flashing high-pressure condensate to atmospheric pressure, it was necessary to water-cool the pipe, *k*, leading from the trap to the weigh tank, *m*. The still was operated in the normal manner for 5 or 6 hours to establish uniform temperature conditions before measurements were started. Following this period, all temperature and pressure readings as well as measurements of condensed steam and condensed fatty acids were taken every 15 minutes during the 3 to 5 hour test period. This test covered the middle period of the complete 20-hour run. The stock level in the still was kept as constant as possible. Steam pressure variations were not greater than ±7 pounds per square inch (0.5 kg. per sq. cm.). The temperature of the stock fed and the temperature in the still did not vary more than ±5° F. (2.8° C.). The distillate receiver was pumped empty just before the first readings were taken and again just as the final reading was taken. The distilled fatty acids were measured in another tank.

A blank run was made to determine the amount of heat lost due to convection and radiation. The still was filled with crude fatty acids to the normal level, and the operating temperature was maintained with the high-pressure steam. During this test the vacuum equipment was shut off, and the still held at atmospheric pressure. In this way the normal heat losses from the still occurred but no distillation took place. As in the other runs, these conditions were maintained for 3 or 4 hours to establish equilibrium and then a 4-hour measurement of steam condensate was made and from these measurements the heat loss was calculated.

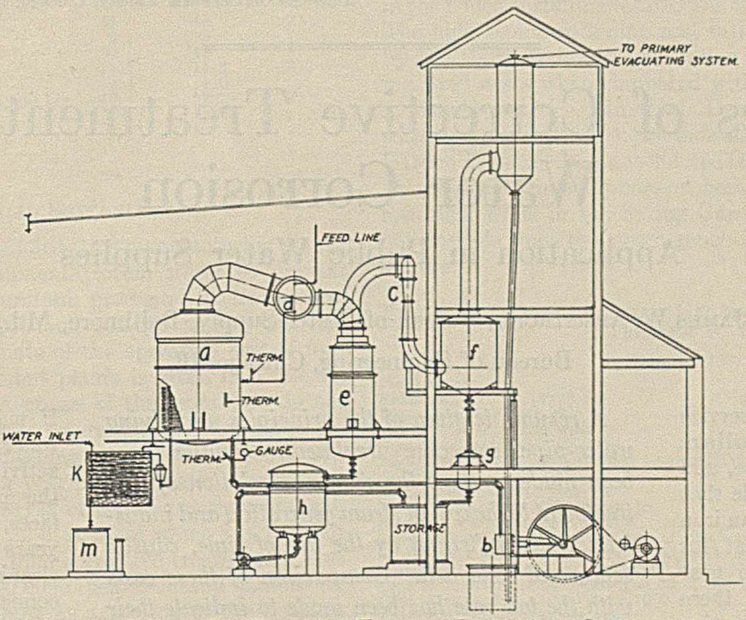


Figure 1. Gensecke Type of Fatty Acid Still

Calculation of Results

The total heat supplied to the still during each test period was calculated from the observed steam pressure, steam temperature, and weight of condensate by use of Keenan's steam tables. No question of steam quality was involved, as in all cases the steam was superheated because of compression from a much lower pressure. There is a possibility of some error in measuring the amount of condensate. If the trap on the condensate end of the heating coil should allow some steam to pass, along with the condensate, the present set-up would have measured it as condensate and caused high results. No evidence of this was found. The radiation and convection test showed a total heat loss from the still of 129,800 B. t. u. (32,550 calories) per hour under operating conditions. This would, of course, vary with weather condition in the still house, but all runs to which this loss is applied were made during a 12-day period in June, during which time the temperature was fairly uniform.

By deducting the heat loss from the total heat supply in the test runs, the total heat per pound of fatty acid can be determined by direct ratio. Part of this heat is used in raising the feed from 353° F. (178° C.) to the still temperature of 432° to 442° F. (222° to 228° C.). In calculating this quantity the recent specific heat data of Lederer (*3*) were used, and it was assumed that the amount of stock fed was just equal to the amount distilled. This may not be strictly true, owing to a small change in gravity of the stock in the still, but the error is small. After deducting the heat loss, the preheat required for raising the feed to distillation temperature, and the heat absorbed by the agitation steam from the total heat supply, the latent heat of vaporization was found. This was 108 B. t. u. per pound (60 calories per gram) for recovered-grease fatty acids and 124 B. t. u. per pound (69.7 calories per gram) for red oil under actual distillation conditions. This seems to indicate that palmitic and stearic acids have a lower latent heat of vaporization than oleic acid. The recovered-grease fatty acid is a mixture of oleic, stearic, and palmitic acids, whereas the red oil is predominantly oleic acid. It is likely that most of the difference is due to the palmitic acid in the grease and not to the stearic acid. Theoretical values of latent heat of vaporization of pure stearic and oleic acids calculated from vapor pressures by Skärblom (*4*) are practically the same, whereas the value for palmitic acid is lower than either.

Conclusion

The present results on red oil are of the same order, it is true, as those on the somewhat similar cottonseed fatty acids obtained by Alsberg. The authors believe however that Alsberg's value is the result of compensating errors. For example, he assumed a specific heat of 0.46 as compared with the 0.60 to 0.66 reported by Lederer, which was used here. This is a serious error, as almost one-fourth of the heat involved is sensible heat and not latent heat of vaporization. In addition, Alsberg estimated his heat loss which is probably much too low, whereas the authors measured their loss. They found nearly 25 per cent of the total heat supplied was lost by radiation and convection from the still pot. Further, experience with the type of still used by Alsberg leads the writers to believe that much of the water he measured was not condensed steam but condenser leakage. Finally the figure obtained here for latent heat of mixed fatty acids from

Table I. Data for Calculating Latent Heat of Fatty Acids

Date Stock distilled	6/24/32 Heat loss	6/16/32 Recovered grease	6/17/32 Recovered grease	6/28/32 Red oil
Length of run, hr.	4	4	3	5
Steam condensed, lb.	625	2,765	2,087	3,804
Steam pressure, lb./sq. in. abs.	440	435	485	455
Steam temp., ° F.	541	511	540	541
Total heat of steam, B. t. u./lb.	1,266	1,247	1,261	1,264
Heat of liquid, B. t. u./lb.	435	434	446	439
Heat available, B. t. u./lb.	831	813	815	825
Total available heat, B. t. u.	519,400	2,247,900	1,700,900	3,138,300
Heat loss, B. t. u.	519,400[a]	519,400	389,400	649,000
Heat taken up by agitation steam, B. t. u.		6,800	5,800	8,700
Heat supplied to fatty acid, B. t. u.	.....	1,721,700	1,305,700	2,480,600
Total distillate, lb.	.....	10,390	7,635	13,500
Feed temp., ° F.	.....	355	352	353
Still temp., ° F.	448	432	442	434
Mean specific heat:				
From 191° F. to feed temp.	.....	0.60	0.60	0.62
From 191° F. to still temp.	.....	0.64	0.65	0.66
Heat required for preheat, B. t. u.	.....	589,000	487,000	808,000
Heat available for vaporization, B. t. u.	.....	1,132,700	818,700	1,674,600
Latent heat of vaporization, B. t. u./lb.	.....	109.0	107.2	124.0

[a] 129,800 B. t. u. per hour.

recovered grease is considerably lower than any others reported, in spite of the fact that any possible errors in these measurements were in the direction of high results.

The latent heat of vaporization will, of course, vary with temperature. However, the temperature range over which it is practical to distill fatty acids and obtain good quality is rather limited, and it is felt that these results will cover most technical needs.

LITERATURE CITED

(1) Alsberg, Julius, IND. ENG. CHEM., 12, 490–3 (1920).
(2) Gensecke, Wilhelm, U. S. Patent 1,713,431 (May 14, 1929); German Patent 545,764 (March 5, 1932).
(3) Lederer, E. L., *Seifensieder-Ztg.*, 57, 329–31 (1930).
(4) Skärblom, K. E., *Arch. Wärmewirt.*, 10, 174–6 (1929).

RECEIVED September 28, 1933. Presented before the meeting of the American Oil Chemists' Society, Chicago, Ill., October 12 to 13, 1933.

Economics of Corrective Treatment for Cold Water Corrosion

Application in Public Water Supplies

EDWARD S. HOPKINS, JAMES W. ARMSTRONG, Bureau of Water Supply, Baltimore, Md., AND JOHN R. BAYLIS, Bureau of Engineering, Chicago, Ill.

A résumé is given of the principles underlying water-pipe corrective treatment. Studies have been made to show the economic relation of this treatment to the cost of steam generation and industrial water softening by the use of lime, caustic soda, and soda ash. Comparison of these costs with the tax rate has been made to indicate their economic distribution between industrial activity and the municipality. The question of soap consumption and pipe renewal by consumers is discussed. Utilizing the data obtained at Baltimore, an estimation of the cost and benefits in a selected group of cities is given. The value of this protection to the pipe system is demonstrated.

THERE are now in service many million dollars worth of iron pipe, and it does not seem probable that a metal less corrosive than iron will be used to any extent for large water pipes in the near future. Consequently, if there is to be a substantial reduction in corrosion, it must be brought about by treatment of the water and not to the use of other materials or more durable pipe coverings. The mains are installed, and, except in places where they are too small or have corroded to the extent that they will no longer withstand the pressure, it would not be economy to replace them by another material, regardless of how cheap the other metal might be. Complete elimination of corrosion is not to be brought about by water treatment, but the value of the reduction where the water is fairly corrosive greatly exceeds the cost of treatment.

It is probably safe to say that no neutral water would be satisfactory to all users in any city, and, if it should be treated to remove the constituent that is objectionable to some users, it would become objectionable to others. In considering the desirability of corrective treatment for water, the question should be determined on the basis of the most good to the majority of consumers.

The formation and continued maintenance of a thin film of calcium carbonate on the inside of pipe as a protective coating for prevention of corrosion results in a number of benefits. Any attempt to evaluate the savings to a distribution system resulting from the use of corrective treatment would be futile without exact cost data extending over a long period of time, because of the many factors not chargeable to corrosion. It would however be a serious matter to permit the corrosion and pitting of the many miles of mains in our cities, which, for Baltimore and vicinity, are valued at over $30,000,000.

The corrosion of mains causes the formation of incrustations and tubercles that greatly increase friction losses and reduce their carrying capacity. In the case of small mains, they may become almost useless unless they are occasionally cleaned. If mains are cleaned and the water not corrected, corrosion activity is increased because of the exposure of fresh iron surfaces, and it will be only a few years before they again require cleaning. The many buildings connected to water supplies are equipped with expensive piping systems of wrought iron, steel, and galvanized iron, which are more readily attacked by corrosive water than cast iron. While it is not possible to determine accurately the cost of corrosion in such systems, it is very great where no provision is made for prevention.

An engineering project is often decided exclusively on the basis of cost. The one estimated to be the cheapest is considered the best. Such decisions omit the source of important factors such as a reasonable assurance of security, a satisfied public, freedom from complaints, and reduced maintenance costs. Should the "soft water" cities omit corrective treatment, the familiar "red water trouble" would cause innumerable complaints from householders regarding the staining of clothes, bathroom fixtures, etc. In addition to the direct replacement cost of pipe due to corrosion, a host of indirect costs would accrue, occasioned by damage to plaster, furniture, and other goods.

While it is not possible to place a material value upon an intangible asset, freedom from complaints and ill feeling is worth much to any community or company and in itself justifies a large monetary outlay.

Corrective treatment in the Baltimore supply was inaugurated in 1922 (*2*) and utilized a pH value of about 8.3, producing a slight "egg shell" precipitate of calcium carbonate in the system as a protective coating on the interior pipe surface. This hydrogen-ion concentration has been gradually reduced because of changing buffer characteristics of the water and regulation by the von Heyer "marble test" (*4*) to a pH value of 7.9. This alkalinity has maintained the coating in good condition. It has been demonstrated (*5*) that water, when initially treated with lime to the calcium carbonate equilibrium point, will hold its pH value after passage through an entire system, including a double set of balancing reservoirs and about 1500 miles of pipe; this proves the practicability of the treatment.

TABLE I. INCREASE IN HARDNESS OF GUNPOWDER RIVER WATER CAUSED BY LIME CORRECTIVE TREATMENT

(Average for 1932 expressed as p. p. m.)

	RIVER WATER	PLANT EFFLUENT	INCREASE
Soap hardness[a]	39	48	9
Noncarbonate alkalinity[a]	2	9	7
Alkalinity[a]	39	42	3
Ca	11.1	14.4	3.3
Mg	4.1	4.0	...
Total hardness calculated from Ca and Mg	44	52	8[b]
CaO applied	..	5	...
CaO calculated as $CaCO_3$	..	9	...

[a] As calcium carbonate.
[b] Or 18.2 per cent.

INDUSTRIAL SOFTENING

As would be expected, laundries, ice manufacturing plants, and certain other establishments soften water to prevent soap loss or to produce a uniform product. These installations range between 100,000 and 500,000 gallons per day capacity. A detailed estimate of the operating cost of four zeolite softeners from different plants is given in Table II. The figures presented are averages of the group and do not represent a single unit. It is believed that these data are typical of the industrial softening in the city. About 30,000,000 gallons of water per year per installation are treated at a total cost per unit of $1128 or $0.038 per thousand gallons for a total hardness of 52 p. p. m. of which 8 p. p. m. or 18.2 per cent is caused by lime corrective treatment. This excess hardness cost is $0.0069 per thousand gallons or $205.30 per year. Considered as a portion of the business overhead, this added cost is a small item.

TABLE II. COST OF SOFTENING WATER WITH ZEOLITES

(Average of four industrial systems for 1932)

Time between regenerations, hr.		7.5
Water softened per regeneration, gal.		114,000
Water used per year, gal.		29,580,000
Regenerations per year		293
Salt per regeneration, lb.		225
Cost of salt at $15.40 per ton		$1.73
Water wasted per regeneration, gal.		7,348
Cost of water at $0.75 per 1000 cu. ft.		$0.74
Labor per regeneration		$0.80
Cost per year for regeneration of zeolite	$873.52	
Depreciation of zeolite (20% of $1038.94)	207.79	
Depreciation of softener (10% of $467.00)	46.70	
Total cost per year	$1128.01[a]	
Cost per 1000 gal.		$0.038
Additional cost per year caused by corrective treatment (18.2%)		$205.30
Additional cost per 1000 gal.		$0.0069

[a] Based upon average values for water of 70 p. p. m. hardness.

Cost data for softening and steam generation at the Point Breeze Plant of the Western Electric Company are shown in Table III. The yearly steam consumption was 192,000,000 pounds for 1932, of which 40 per cent was "make-up" water, at a softening cost of $0.14 per 1000 gallons of water used. Their "blow-down" cost was approximately $0.15 per thousand gallons. The cost of softening water in the boiler, including return, was $0.06 per thousand gallons. The high zeolite softening cost in this installation is caused by the short cycle of regeneration (18,000 gallons) increasing fixed costs when compared with that obtained in other industrial practice. In 1927 Powell (7) reported zeolite softening costs of $0.04 per thousand gallons for the Spring Garden Plant of the Consolidated Gas and Electric Company. In the plant under discussion here, 60 per cent of water is returned, while in the Spring Garden plant recirculation is not possible since the steam generated is used for gas manufacture.

TABLE III. COST OF STEAM GENERATION, USING CORRECTED TREATED WATER

(Data for 1932)

Plant horsepower	2,715
Rating at 200° C. (392° F.)	94,012
Water used for year, gal.	9,219,000
Yearly cost softening with zeolite	$1,288.72
Cost of softening per 1000 gal.	$0.14
Additional cost of softening due to corrective treatment (18.2%)	$233.55
Additional cost per 1000 gal.	$0.025
Steam generated for year, lb.	192,000,000
Make-up water at 60% return, lb.	76,800,000
Make-up water for year, lb.	9,219,000
Solids per year at 71 p. p. m. (av. of city water), lb.	5,453
Additional solids caused by lime treatment (8 p. p. m. or 11.3%), lb.	614
Water as blow-down per day at 600 lb./hr., lb.	14,400
Cost of heat loss in blow-down at $0.25 per 1000 lb.	$3.60
Cost of water lost at $0.75 per 1000 cu. ft.	$0.17
Total blow-down cost per year	$1,376.05
Blow-down cost per 1000 gal.	$0.149
Increased cost per year of blow-down caused by corrective treatment or 4.5%	$61.92
Increased cost per year per 1000 gal.	$0.007
Total cost for treatment caused by added hardness	$295.47
Additional cost per 1000 gal. for added hardness	$0.032
Additional cost per 1000 lb. of steam	$0.001

In consideration of these facts, the increased cost caused by the lime treatment is $0.03 per thousand gallons of make-up water or $295.47 per year. The total industrial horsepower used by steam generation is not obtainable for Baltimore or any other city with accuracy. It is impractical, therefore, to compare steam generating costs in one plant with any other plant, since varying amounts are used in processes, lost in lines (whether heat exchangers are used or not), varying make-up proportions, and other factors. Therefore, it

TABLE IV. SOAP WASTE CAUSED BY ADDED HARDNESS DUE TO CORRECTIVE LIME TREATMENT

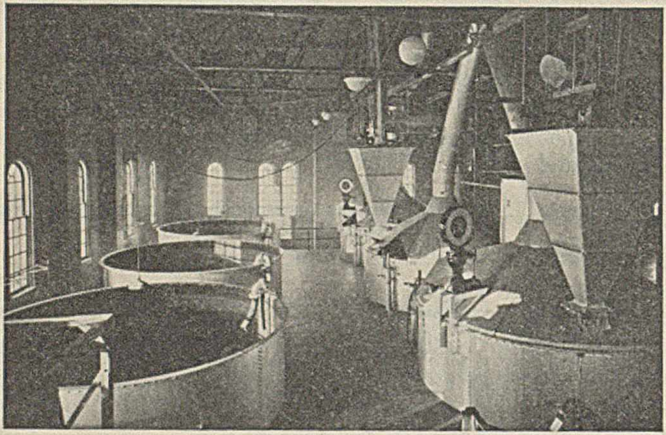
(Data obtained by test of twenty-five different brands)

	UNCORRECTED WATER (HARDNESS, 36 P. P. M.)				CORRECTED WATER (HARDNESS, 49 P. P. M.)				SOAP WASTE CAUSED BY 13 P. P. M. ADDED HARDNESS		
SOAP	*Grams per liter*	*Lb. per 1000 gal. per p. p. m.*	*Gal. softened per lb.*	*Cost per gal.*	*Grams per liter*	*Lb. per 1000 gal. per p. p. m.*	*Gal. softened per lb.*	*Cost per gal.*	*Grams per liter*	*Gal. softened per lb.*	*Cost per gal.*
Toilet	0.34		352	$0.0014	0.39		307	$0.0016	0.05	45	$0.0002
	0.42		281	0.0026	0.52		230	0.0032	0.10	51	0.0006
	0.46		261	0.0006	0.56		214	0.0007	0.10	47	0.0001
	0.47		255	0.0018	0.58		207	0.0021	0.11	48	0.0003
	0.49		245	0.0019	0.60		198	0.0024	0.11	47	0.0005
	0.46		261	0.0018	0.58		206	0.0023	0.12	55	0.0005
	0.50		242	0.0017	0.62		193	0.0021	0.12	49	0.0004
	0.46		261	0.0017	0.59		203	0.0021	0.13	58	0.0004
	0.49		245	0.0056	0.62		193	0.0071	0.13	52	0.0015
	0.49		245	0.0017	0.62		193	0.0022	0.13	52	0.0005
	0.50		240	0.0008	0.65		184	0.0010	0.15	56	0.0002
	0.49		245	0.0107	0.67		179	0.0148	0.18	66	0.0041
Average	0.46	0.11	261	0.0027	0.58	0.10	209	0.0035	0.12	52	0.0008
Glycerol	0.58		206	0.0046	0.70		171	0.0056	0.12	59	0.0010
	1.01		118	0.0050	1.35		89	0.0067	0.34	71	0.0017
Average	0.80	0.17	162	0.0048	1.02	0.16	130	0.0062	0.22	65	0.0014
Kitchen	0.90		132	0.0006	0.99		121	0.0006	0.09	11	0.0001
	0.96		126	0.0006	1.08		110	0.0007	0.12	16	0.0001
	1.14		104	0.0019	1.33		90	0.0022	0.17	14	0.0003
	0.90		132	0.0006	1.21		99	0.0007	0.31	33	0.0002
Average	0.98	0.23	123	0.0009	1.14	0.19	105	0.0011	0.16	18	0.0002
Soap powder	0.75		159	0.0009	0.80		151	0.0009	0.05	8	0.0001
	0.47		255	0.0007	0.55		218	0.0008	0.08	37	0.0001
Average	0.61	0.13	207	0.0008	0.67	0.11	185	0.0009	0.06	23	0.0001
Scouring powder	17.14		7	0.0162	21.45		6	0.0203	4.31	1	0.0041

is impossible to draw economic conclusions predicated upon any given plant as characteristic conditions for a community.

Soap Waste Cost

In an effort to obtain some idea of the soap waste caused by corrective treatment, a study was conducted to determine the softening value of various commercial brands of soap and soap powders. As presented in Table IV, the added hardness caused by lime treatment produced a soap waste increase varying from 0.05 to 0.34 gram per liter for toilet soaps, 0.09 to 0.31 gram for kitchen soaps, and 0.05 to 0.08 gram for soap powders. The most popular brands of toilet soaps ranged from 0.10 to 0.15 gram per liter. These tests were conducted with alcoholic solutions of the soaps using 50 cc. of water with an equivalent hardness to the city water at the time of testing and were carefully made. This was necessary since it was not possible to obtain sufficient information from the literature, as most studies reported therein were made for the purpose of deciding greater hardness differences and could not be applied. The cost of soap waste caused by corrective treatment varied from $0.0001 to $0.0041 per gallon, depending upon the brand of soap used. When evaluating these costs in relation to soap waste, it must be remembered that many soaps are soft in texture and disintegrate upon standing in the dish, producing excess loss not chargeable to that caused by the water. It is therefore recognized that evaluation of general soap costs cannot be made with accuracy, but specific brands under controlled conditions can give a reasonable estimate of this expense to a family.



Liquid Alum Manufacturing Plant, Montebello Filters, Baltimore, Md.

As a method of studying soap costs, carefully controlled use of water was maintained in one home of two people for a period of 15 days. All water for cooking, toilet flushing, and sprinkling was noted, and the residue from the total applied to washing. General flat laundry work was done commercially elsewhere and is excluded from consideration. Included in this consumption was a daily bath per person. Detailed data given in Table V disclose that 5.3 gallons of water per person per day were completely softened with soap. This amount is lower than that obtained by Snyder (*8*) of 8 gallons per person in her study of conditions in Columbus, Ohio, probably because she gave data on a family of five including two small children.

This study indicates that about 1934 gallons per person per year are used for washing, with a soap waste caused by corrective treatment of 1.04 pounds per thousand gallons at a total cost $0.19 or $0.024 per p. p. m. of hardness per thousand gallons. This amount probably represents the maximum soap used per person as daily bathing is not characteristic of large population areas; therefore, the average soap consumption per person would be considerably lowered. Hudson and Buswell (*6*) give the per capita soap consumption for several cities in which the hardness of the waters varies considerably. These data indicate that each p. p. m. of hardness caused a per capita increased soap cost of about $0.01 per year. The above values were computed upon the usual retail price, and, since in most households soaps are purchased at reduced rates, it is obvious that these costs are somewhat higher than actually found in practice.

Emphasis must be placed upon the fact that the above data cannot be accepted as conclusive, except for the particular test. The cost data assumptions presented should, therefore, be taken only in very general terms, but they do show that the family expense for corrective treatment in terms of soap waste is slight. The savings effected in pipe repair and maintenance by the prevention of corrosion more than compensate for the excess soap cost.

This problem is quite different from that of the excess soap waste cost found in the "hard-water" cities in certain parts of this country. Comparison of soap waste caused by waters of varying hardness, on the basis of pounds per p. p. m. per thousand gallons, discloses unrelated values, since it is well recognized that a certain minimum quantity of soap is necessary to produce a lather even with distilled water. Waters high in calcium and magnesium salts give the lowest soap loss per p. p. m., indicating that this minimum concentration has an important bearing upon the total result. Therefore, it is clear that soap waste values above this minimum are comparable but, if based upon the total hardness, may be erroneous. This can be explained by reviewing the colloidal chemical factors involved in the shaking test.

Table V. Household Soap Consumption

Period of test, days	15
Persons in family	2
Water for flushing toilets, gal.	948
Water for cooking, gal.	94
Water for sprinkling lawn, gal.	557
Water for washing (flat work laundry excluded), gal.	516
Total water used, gal.	2115
Water per person per day for washing, gal.	17.2
Soap used at 49 p. p. m. hardness for 516 gal. of water,[a] gal.	1.02
Soap per 1000 gal.,[a] lb.	1.97
Soap per 1000 gal. per p. p. m. hardness,[a] lb.	0.04
Soap waste per 1000 gal. per p. p. m. at 49 p. p. m. hardness, from Table IV, lb.	0.13
% of completely softened water by soap used in household	30.8
Equivalent water per person per day, gal.	5.3
Soap wasted per 1000 gal. for 8 p. p. m. added hardness, lb.	1.04
Soap waste cost per person per day for 8 p. p. m. added hardness	$0.00098

[a] Toilet soap, %	17.4
Kitchen soap, %	32.2
Soap powder, %	50.4
	100.0

The final solution contains colloidal particles of insoluble calcium and magnesium soaps. As shown by Briggs (*3*), there is a relationship between the amount of soap in the interface and that still peptized in the water. It is a case of distribution of soap between the water and the interface. Bancroft (*1*) points out that there "will be some ratio of calcium to sodium at which the two oleates will practically balance each other, and the slightest relative change will change the type of emulsion." Since a foam is controlled by similar laws, this relative change explains the slightly different analytical results obtained by a group of people with the same water, owing to the intensity of shaking developed by the individual. He also states: "To get a fairly permanent foam, the surface film must either be viscous in itself or must be stabilized in some way. This can be done by introducing a solid powder into the interface." This is precisely what occurs when making the soap test for hardness, assuming the

TABLE VI. COMPARATIVE NEUTRALIZATION COST OF CARBON DIOXIDE BY LIME AND SODIUM COMPOUNDS

(Taxable basis of city for 1932, $188,934,444; 1 cent of tax rate at $2.65 per $100 produces $105,490.35)

LABORATORY DATA WITH UNCORRECTED FILTERED WATER CONTAINING 11.4 P. P. M. CO_2 AT pH OF 6.4				DATA BASED UPON PUMPAGE AT MONTEBELLO FILTERS FOR 1932, 130,380,000 GAL.			
TO OBTAIN A pH VALUE OF:	COMPOUND	P. P. M. NEEDED	P. P. M. HARDNESS INCREASE	COMPOUND	TOTAL COST	COST PER MILLION GAL.	INCREASE IN TAX RATE DUE TO TREATMENT
				Tons			
7.9	CaO	5.5	7	1,163.666	$7,912.93	$0.21	$0.0008
	NaOH	8.9	0	1,811.102	98,161.73	2.64	0.0093
	Na_2CO_3	22.2	0	5,919.235	161,004.55	4.33	0.0153
8.2	CaO	6.1	11	1,290.577	8,775.92	0.24	0.0008
	NaOH	9.4	0	1,912.806	103,674.09	2.79	0.0098
	Na_2CO_3	24.8	0	6,611.184	179,824.15	4.84	0.0170
8.5	CaO	7.2	13	1,523.304	10,358.47	0.28	0.0010
	NaOH	10.3	0	2,095.947	113,600.33	3.07	0.0108
	Na_2CO_2	27.3	0	7,277.634	197,951.64	5.33	0.0188

solid colloidal oleate particles are introduced into the interface, thus stabilizing the foam. It is easily conceived that, with different concentrations and intensity of shaking, the amount so adsorbed may vary within wide limits, thereby explaining the divergence of results reported in the literature.

USE OF SODIUM COMPOUNDS TO REDUCE CARBON DIOXIDE

Neutralization of free carbon dioxide is practical with either caustic soda or soda ash to maintain a calcium carbonate film within the pipe system, but it is usually not economical for the production of such a film. The only justification for such treatment would be to prevent the slight hardness increase caused by lime, thereby increasing the efficiency of steam generating plants with resultant slight savings in their softening processes. But, since natural waters always contain a certain minimum of hardness, softening to a greater or less degree must be practiced everywhere.

Maintenance of pH values in the Gunpowder River (Md.) water between 7.9 and 8.5, which is the calcium carbonate equilibrium point, requires from 8 to 10 p. p. m. of caustic soda and from 20 to 30 p. p. m. of soda ash to protect a previously formed film. To precipitate a calcium carbonate film would require from 12 to 15 p. p. m. of caustic soda and from 30 to 40 p. p. m. of soda ash. This would be costly, and, if these materials were used, only neutralization should be undertaken with precipitation of any needed coating by lime. The data for this conclusion are presented in Table VI. Converting these facts into money values, it is evident that to neutralize 11.4 p. p. m. of carbon dioxide to a pH value of 7.9 will cost, based upon 1932 pumpage, $98,000 if solid caustic soda is used and $161,000 if soda ash is used. These costs would increase the tax rate $0.93 per $100 of assessment for caustic soda and $1.53 for soda ash. The purification cost would be increased $2.64 per million gallons for caustic soda and $4.33 for soda ash as compared with $0.21 for equivalent lime treatment.

Translating these values to the economic life of the community as shown in Table VII, it is demonstrated that utilization of sodium compounds in comparison with lime, for corrective treatment, is not practical. However, when reviewing these data, it must be remembered that the only accurate comparable figures are those obtained in laundry practice. As previously stated, the many variable factors controlling the use of steam, together with erratic consumption of soap, make these values unreliable except in the particular plant or home. They are offered in Table VII simply as an index for comparison, with full recognition of the fact that they are not generally applicable.

SOUTH FILTER GALLERY, OLD PLANT, MONTEBELLO FILTERS

TABLE VII. COMPARISON OF APPROXIMATE SOFTENING COSTS CAUSED BY LIME CORRECTIVE TREATMENT WITH INCREASED TAXES IMPOSED BY SUBSTITUTION OF CAUSTIC SODA

(Based upon a tax rate of $2.65 per $100 assessment, and hardness of 8 p. p. m.)

PROPERTY	ASSESSABLE BASIS	TAX INCREASE FOR NaOH TREATMENT	ADDED YEARLY SOFTENING COST CAUSED BY CaO TREATMENT	TYPE OF SOFTENING
5 steam plants	$20,546,620	$1,684.28	$1,477.35	Zeolite
4 laundries	479,040	41.20	812.20	Zeolite
Home[a]	5,000	0.41	1.40[b] 0.35[c]	Soap

[a] Family of 4.4 persons.

[b] Probable maximum per family.

[c] Computed from Hudson and Buswell's data (*6*), considered the most nearly accurate for large population areas.

TABLE VIII. HYPOTHETICAL COST OF CORRECTIVE TREATMENT OF WATER IN VARIOUS CITIES SHOULD LIME BE REPLACED BY CAUSTIC SODA

CITY	pH	CaO USED	INCREASED SOAP HARDNESS	EQUIVALENT NaOH	APPROX. INCREASED COST PER MILLION GAL.
		P. p. m.		*P. p. m.*	
Akron, Ohio	7.9	6.6	10	9.4	$2.89
Atlanta, Ga.	7.6	4.1	11	5.8	1.78
Baltimore, Md.	7.9	5.0	9	7.1	2.18
Birmingham, Ala.	7.2	9.4	2	13.3	4.08
Cambridge, Mass.	8.6	10.6	13	15.1	4.64
Clarksburg, W. Va.	8.0	22.2	17	31.5	9.57
Hagerstown, Md.	7.8	7.8	5	11.1	3.41
Louisville, Ky.	8.0	6.1	5	8.7	2.67
Philadelphia, Pa.	7.0	7.5	6	10.7	3.28
Washington, D. C.	7.8	10.3	11	14.6	4.48

Comparative cost data for several cities, assuming corrosion control by use of caustic soda, are shown in Table VIII. In most instances excessive expense would be incurred by the municipality for this treatment.

CONCLUSIONS

The data and findings of this paper are applicable only to waters in which the total hardness does not exceed 75 p. p. m.

The cost of corrective treatment with lime for corrosive waters of this type is amply justified for an entire community.

The cost of treating water with caustic soda for the neutralization of carbon dioxide, thereby preventing corrosion with avoidance of an increase in hardness, in order to reduce soap consumption and save expense in preparing boiler feed water is not justified in a public water supply of this type.

The cost to steam generating plants for the treatment of boiler feed water to overcome the excessive hardness due to lime treatment is about equal to the additional taxes they would have to pay should the entire city supply be treated with caustic soda. This ratio would vary with local conditions in a given community.

Laundries would generally be direct gainers by the caustic soda treatment, but, as their increased cost is small, there can be no justification in taxing an entire community for the benefit of a few.

The increased burden to the householder for caustic soda treatment would in most instances be about equal to the present soap waste cost caused by lime treatment. This ratio is, of course, governed by the individual use of water for washing purposes. As a considerable amount of soap is discarded in household use, any exact financial saving cannot be determined.

Economic consideration necessarily based upon more or less indefinite data indicates that the great expense of caustic soda treatment is not justified to the municipality. The cost of treating water at the plant to prevent corrosion, together with other costs to the consumer, is but a small fraction of the losses sustained should corrosive water be supplied. It is therefore believed that corrective treatment with lime produces a water of the most economic value to the most users.

ACKNOWLEDGMENT

The data given in Table III were obtained through the courtesy of A. A. Ewing, assistant superintendent of the Point Breeze Plant of the Western Electric Company.

LITERATURE CITED

(1) Bancroft, W. D., "Applied Colloidal Chemistry," 3rd ed., p. 375, McGraw-Hill, 1932.
(2) Baylis, J. R., *J. Am. Water Works Assoc.*, 9, 408 (1922).
(3) Briggs, T. R., *J. Phys. Chem.*, 19, 2110 (1915).
(4) Heyer, von, Tillmans, and Heublein, "Die Untersuchung und Beurteilung des Wassers und Abwassers," 4th ed., p. 40, Ohmuller u. Spitta, 1915.
(5) Hopkins, E. S., IND. ENG. CHEM., 25, 1050 (1933).
(6) Hudson, H. W., and Buswell, A. M., *J. Am. Water Works Assoc.*, 24, 859 (1932).
(7) Powell, S. T., "Boiler Feed Water Purification," p. 122, McGraw-Hill, 1927.
(8) Snyder, Pauline, Thesis, Ohio State University, 1927.

RECEIVED September 26, 1933. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.

Corrosion Inhibition by Lime Treatment

Effect on Industrial Water-Consumption Costs

SHEPPARD T. POWELL, 330 N. Charles St., Baltimore, Md.

THE corrosion of water mains and service pipes resulting in "red water" has been a perplexing and costly problem in the operation of many municipal and privately owned water systems. Up to the present, the only relatively satisfactory method for inhibiting this condition has been the addition of sufficient quantities of lime to produce protective coatings on the inside of the mains and laterals of the distribution systems. The classical studies by Baylis, Hoover, Hopkins and other investigators has added greatly to our knowledge on this subject.

The success of anticorrosion treatment by lime will depend largely on the intelligence of the operators in the proper adjustments to meet local operating conditions. Fundamentally the theory of protective coatings to inhibit corrosion is sound, and assured success will be forthcoming if the rate of scale deposition can be adequately controlled. The difficulty that was experienced in the earlier periods of treatment was due largely to a lack of adequate control procedure, and there are many instances where inadequate treatment has resulted in excessively costly operation. There are numerous instances where the pipe line deposits have built up to such an extent as to impose excessive pumping charges resulting from the diminution of the size of the mains. The ideal conditions for the prevention of corrosion by lime treatment is to secure an impermeable film of calcium carbonate and to adjust the treatment after the deposit has been produced so as not to dissolve the deposit already formed and to hold further deposition of calcium carbonate at a minimum. To produce these conditions requires extensive experience and constant accurate control of the treatment. Without such control, inadequate treatment will result, placing a heavy burden on both the domestic and industrial users of the water supply so treated.

Although many public water supplies now receive lime treatment to inhibit "red water," little, if any, thought has been given to the economic phases of the problem. To most investigators and to water works officials generally, the availability of a method for controlling "red water" has been the impelling motive for inaugurating the treatment, irrespective of any detrimental effect resulting therefrom for service other than purely domestic. Wherever the cost of treatment has been given consideration, the factors considered have been limited to the actual cost of chemicals used and to the capital investment for equipment necessary to apply the lime. Further, the savings resulting from the reduction in pipe renewals have been fully credited to the treatment. Financial losses to industrial users resulting from this form of treatment have been given scant consideration, although in some cases, especially where overtreatment has occurred, the burden on the industrial users has been very great. It is the purpose of the author's comments merely to draw attention to these facts in the hope that, where such treatment is under consideration or now in use, consideration be given to the industrial consumer's status.

SCALE FORMATION

Possibly the most direct and calculable losses from the industrial user's viewpoint are those sustained by the increased scale-forming solids added to the water and the financial losses incurred in steam generation. These are tangible losses subject to accurate estimates. From a recent study in one plant it was demonstrated that lime treatment of the public water supply which was used for make-up water imposed an additional cost for treatment of $15.04 per million gallons of water used, or approximately $1500 annually for the plant in question. It is interesting to note in this connection that the amount of residual lime in the city water resulting from the anticorrosion treatment was only a half-grain per gallon. The itemized losses at the plant in question have been summarized in Table I. These figures are reliable, since the company maintains an accurate accounting system, but are probably lower than the actual losses sustained, since there are a number of intangible losses which may not be readily evaluated and, therefore, have not been given consideration in the figures reported. It is readily apparent that in a highly industrialized community, where large quantities of water are used for steam generating purposes, the total annual losses may run into large figures.

TABLE I. SUMMARY OF INCREASED COST OF OPERATION OF ZEOLITE WATER SOFTENING DUE TO INCREASING THE HARDNESS OF THE CITY WATER ONE-HALF GRAIN PER GALLON

	ADDED COST PER MILLION GALLONS OF BOILER FEED MAKEUP
A. Increase in salt consumption	$1.50
B. Increased sodium sulfate required to correct the ratios	0.99
C. Fuel losses due to increased boiler blow-down	1.88
D. Cost of city water required for increased zeolite backwashing and boiler blow-down	5.48
E. Increased depreciation and maintenance	2.05
F. Increased labor	3.14
	15.04
Increased cost (disregarding items C, E, F)	7.97

INCREASED SOAP CONSUMPTION

Possibly the greatest single financial burden on a community from lime treatment is the increased soap consumption resulting from the added residual lime in the treated supply. It is difficult to estimate these losses accurately, but even the most conservative calculation will demonstrate that the cost of soap consumed is an important item and may not be ignored in evaluating the actual cost of anticorrosion prevention measures as now practiced by municipalities.

Various investigators have shown that each part per million of hardness added to the water will increase the soap consumption from 0.07 to 0.3 pound per thousand gallons of water treated. Undoubtedly the figures in the upper range are excessive, and the actual amount is close to 0.15 pound; this is the factor used in the author's estimate. This figure closely approximates the results obtained by the previous authors who have established a figure of 0.13 pound. Assuming the average cost of soap at 15 cents per pound, this would amount to $360 per million gallons of water used for washing purposes for each grain of increased hardness. It is readily apparent that in large communities such losses may not be ignored in an intelligent estimate of the value of such treatment as it affects the taxpayer.

FINANCIAL LOSS DUE TO INCREASED HARDNESS

The penalty imposed on industrial users will vary greatly with the specific requirement of the processes affected. A short time ago the writer was consulted by a large textile industry relative to the effect of the use of water from a municipal water supply where lime treatment for the prevention of "red water" is practiced. Difficulty in processing was encountered shortly after the correction treatment was undertaken. This study revealed the fact that continued use of the municipal supply would result in completely disrupting the process and would impose a great financial loss annually on the manufacturer. It was necessary to secure a new water supply requiring a capital expenditure of approximately $50,000. In addition to this burden on the consumer, the water company lost several thousand dollars revenue annually by discontinuance of service to one of its largest consumers. Such cases are by no means rare but are seldom reported in discussing the merits and cost of lime treatment.

The importance of this problem to industries was demonstrated in an experience in a highly industrialized textile community in the East within the past two years. Immediately after the lime treatment of the public water supply started, complaints were received from silk dyers. The magnitude of the troubles resulting varied in different plants, but all appeared to be more or less seriously affected. The major complaints resulting from the difficulties in the tin weighting of silk were due to the detrimental action of high alkalinity, increasing the rapidity at which the tin salt deposited and thereby upsetting the normal functioning of this process. Adjustment of the pH value of the water by acid treatment corrected the difficulty in some plants, but at other factories these corrective measures were difficult to adjust on account of specific local operating conditions. The ultimate solution of the problem was effected by furnishing all the industries involved, with water from another supply which was not lime-treated. This procedure, however, was costly and required the construction of large industrial water mains and the incurrence of other incidental losses in making the necessary change from one water supply to the other.

In the final analysis, the matter reverts to the preferential rights of the domestic or industrial consumers. It must be conceded that the first duty of any water company, either privately or municipally controlled, is to furnish a safe water. In this respect the industrial consumers requirement should be given secondary consideration. The desire to produce a potable water should not be construed, however, as is so often the case, to mean that the industrial consumer has no rights and should be penalized unduly to meet the primary requirement. Careful analysis of these conditions in many cases will reveal the fact that no attempt has been made to synchronize the divergent water specifications for the two classes of consumers. The problem is difficult but not beyond equitable adjustment. It may not be corrected, however, if the industrial consumers' requirements are completely ignored and will not be relieved until there are made available comprehensive cost data on this form of treatment. Up to the present, the majority of technical papers which have been presented by various groups interested in the matter have almost entirely ignored the ultimate effect of such treatment other than to direct attention to the success of the treatment in inhibiting "red water" and estimating intangible savings from predicted pipe losses.

RECEIVED November 8, 1933. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.

WORLD NITROGEN SITUATION. Following two years of decreases, the world consumption of nitrogen advanced almost 13 per cent in the fertilizer year ended June 30, 1933, as compared with 1931–32, according to the annual report of the British Sulphate of Ammonia Federation. The production in Chile decreased over 58 per cent, while the output in other countries increased by 12.5 per cent, making a net world increase of 5 per cent.

The total nitrogen-producing capacity in the world at the present time is estimated to be approximately 3,460,000 tons of nitrogen, exclusive of Chile. The "manufactured nitrogen" industry of the world thus operated at an average of about 46 per cent of capacity.

Agreements with the most important Continental nitrogen-producing concerns and a tentative agreement with the Chilean nitrate industry were concluded in July 1932, and as a result orderly selling was introduced into most of the world's markets; these agreements have been continued for 1933–34.

Potash and Alumina from Georgia Shale

S. L. Madorsky

Fertilizer and Fixed Nitrogen Investigations, Bureau of Chemistry and Soils, Washington, D. C.

In the chemical extraction of potash from shales, as typified by the extensive Georgia shales, containing 7 to 8 per cent potassium oxide, the separation of alumina as a by-product enhances the economic potentialities of the operation. In the present paper are described some studies of the separation of alumina in pure form from the other constituents of that mineral rendered soluble by a hydrochloric acid extraction. Subjecting the mixed chlorides to a heat treatment in an atmosphere of hydrochloric acid gas converts the aluminum chloride to the oxide, the other constituents remaining as the water-soluble chlorides.

THE large shale deposit near Cartersville, Ga., represents an important potential source of potash, provided an economical method can be found for its treatment. It is a potassium aluminum silicate, carrying an average of 7 to 8 per cent potash. Various methods, such as volatilization of potash as potassium chloride from the rock at high temperatures (*7*) and extraction of the rock with acids (*2, 12*), have been suggested for the recovery of potash from potassium aluminum silicates. In these methods stress is laid either on recovery of potash as a by-product in cement manufacture or on the recovery of alumina as a by-product. This paper deals with certain reactions involved in the hydrochloric acid extraction of Georgia shale and the separation of alumina in pure form from the extract.

The Georgia shale used in the experiments had the following composition:

	%		%
SiO_2	56.60	MgO	4.00
Al_2O_3	20.53	CaO	0.31
Fe_2O_3	7.01	Loss on ignition	4.31
K_2O	7.13		

The shale was ground to pass a 100-mesh screen and treated with boiling concentrated hydrochloric acid. The liquor was filtered off from the insoluble residue, mostly silica, for use in the following series of experiments, designed as a systematic study of methods of obtaining pure alumina from a mixture of chlorides.

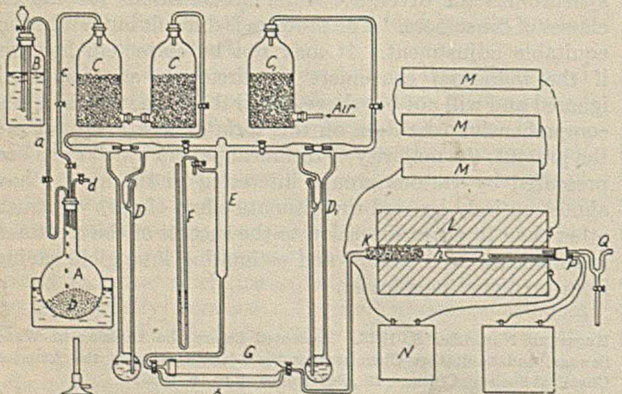


Figure 1. Diagram of Apparatus

The hydrochloric acid extract of Georgia shale contains the following chlorides: potassium, calcium, magnesium, ferric, and aluminum; since all of them are readily soluble in water, a separation by fractional crystallization would be difficult. It is well known that, with the exception of potassium chloride, all of these chlorides decompose when their hydrates are heated in air. This would furnish a means of separating the potassium chloride from the other chlorides by simply evaporating the hydrochloric acid extract to dryness and heating until the unstable chlorides decomposed into oxides, followed by leaching to recover potassium chloride. However, this treatment would throw together the iron and aluminum oxides, and it would be difficult to separate the alumina in pure form, unless by the Bayer process.

The literature on the decomposition of calcium, magnesium, ferric, and aluminum chlorides by heat discloses that, when the heating is done in an atmosphere of hydrochloric acid, the calcium, magnesium, and ferric chlorides can be dehydrated without decomposition, while aluminum chloride is converted into the oxide (*3–6, 8, 11, 13, 14*). Thus, it would appear that by evaporating the Georgia shale extract at about 100° C. until most of the water distills off and then heating the mixture of salts in an atmosphere of hydrochloric acid to remove the remaining water, the residue would consist of a mixture of potassium, calcium, magnesium, and ferric chlorides, and alumina. Of the chlorides, ferric chloride sublimes at 314° C. (*8*), while potassium, calcium, and magnesium chlorides have very high boiling points. By continuing the heating of the residue above 300° C., in an atmosphere of hydrochloric acid gas, the ferric chloride should sublime. On leaching the residue after the volatilization of the ferric chloride, the potassium, calcium, and magnesium chlorides would dissolve, leaving the alumina in pure form. The potassium chloride could then be separated from the other salts by fractional crystallization. This method of recovering potassium chloride and alumina from the Georgia shale extract and of separating pure alumina from a solution of alumina and ferric chlorides, in general, has been tested in a series of experiments described below.

APPARATUS

A diagram of the apparatus used in these experiments is shown in Figure 1.

Hydrochloric acid gas is generated in the flask *A* by dropping concentrated sulfuric acid, coming from bottle *B* through siphon *a*, on sodium chloride *b*. The hydrochloric acid gas passes from *A* through tube *c* into bottles *C* filled with anhydrous calcium chloride. After passing through two beds of calcium chloride, the hydrochloric acid gas passes through flowmeter *D* and mixer *E* into a large tube, *G*, packed with glass wool and P_2O_5. In some experiments, instead of P_2O_5, other drying agents such as anhydrone were used. These drying agents were kept in a bottle. In those experiments where a mixture of hydrochloric acid gas and air was used, the air was first led into bottle C_1, through a bed of calcium chloride, and from there through flowmeter D_1, into tube *E* where it became mixed with the hydrochloric acid gas. It was found in the course of the work that drying of the gases was not essential and was abandoned. The manometer *F* was used for observing the pressure inside the apparatus, which was usually less than 1 cm. of mercury. The flowmeters and the manometer were filled with Nujol. The gas passed from drier *G* into the Pyrex glass tube *K*. In experiments made at high temperatures of about 600° C., the Pyrex glass tube was replaced by a fused quartz tube. The tube *K* was partly filled with broken quartz to preheat the gas before it reached the platinum boat, *h*. The salts were contained in *h*. The temperature of the flowing gas was measured by means of a platinum–platinum rhodium thermocouple, *P*, placed inside a glass tube. The gas escaped through the tube *Q* provided with an outlet for the condensed water. The ferric chloride sublimed from *h* was carried in the hydrochloric acid gas stream and deposited in a tube. The nichrome-wound furnace, *L*, was controlled by a series of rheostats, *M*, and an ammeter, *N*.

SEPARATION OF ALUMINA FROM A SOLUTION OF ALUMINUM AND FERRIC CHLORIDES

Obviously the main problem consists in separating the alumina in pure form, while the recovery of potassium chloride presents no serious difficulties. A series of experiments was first carried out on pure aluminum and ferric chlorides. Separate solutions of these chlorides prepared from C. P. anhydrous aluminum chloride and C. P. hydrated ferric chloride, contained, respectively, 0.4690 gram of aluminum chloride and 0.1590 gram of ferric chloride per 5 cc. of solution. In each experiment, 5 cc. of each solution were placed in the platinum boat, *h*, and evaporated to apparent dryness in an oven at 65° to 75° C. The boat was then transferred to the tube *G* at a temperature of 100° to 110° C., the stream of hydrochloric acid gas started, and the temperature raised first slowly and then rapidly, as follows: In the first 240 minutes the temperature was raised to 180°. By this time most of the water evaporated from the boat. In the interval 240 to 320 minutes, the temperature was raised quickly to the desired point, and for the next 80 minutes it was kept constant at that point. In every case the rate of flow of hydrochloric acid was 300 cc. per minute. In those cases where air was mixed with the hydrochloric acid, the rate was 150 cc. hydrochloric acid and 150 cc. air per minute. The results of these experiments are shown in Table I. In experiment 2, 5 cc. of ferric chloride solution alone, and in experiment 3, 5 cc. of aluminum chloride solution alone were used. Table I shows that, when heated separately (experiments 2 and 3) to 265° C., most of the aluminum chloride decomposes into alumina, while most of the ferric chloride becomes dehydrated and volatilizes, but, when the two chlorides are mixed, a higher temperature is required to effect a separation by this method. At 485° C. the separation is almost complete. Admixture of air to the hydrochloric acid gas did not seem to affect the results to any considerable extent.

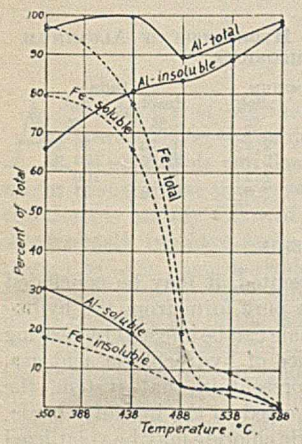


FIGURE 2. SOLUBLE AND INSOLUBLE ALUMINUM AND IRON IN RESIDUE OF GEORGIA SHALE EXTRACT

TABLE I. ALUMINUM AND IRON IN THE RESIDUE OF MIXTURES OF ALUMINUM AND FERRIC CHLORIDES

		Ratio	Aluminum			Iron		
Expt.	Temp.	HCl:Air	Insol.	Sol.	Total	Insol.	Sol.	Total
	° C.		%	%	%	%	%	%
1	248	100:0	68.13	29.20	97.35	5.68	10.21	15.89
2	265	50:50	...	...	....	1.38	4.21	5.59
3	265	50:50	89.06	16.80	105.86	...	...	...
4	265	50:50	86.48	14.50	100.98	11.82	7.61	19.43
5	265	50:50	70.26	25.00	95.26	21.32	7.30	28.62
6	353	50:50	90.66	10.30	100.96	2.29	.63	2.92
7	353	100:0	76.52	19.03	95.55	1.19	.63	1.82
8	350	100:0	96.07	8.55	104.62	1.07	10.88	11.95
9	485	50:50	94.37	5.61	99.98	2.52	.31	2.83
10	485	100:0	95.72	6.16	101.88	0.35	.11	0.46
11	485	100:0	94.41	5.93	100.34	3.08	0.94	4.02
12	485	100:0	92.64	4.12	96.76	1.09	0.27	1.36
13	485	100:0	89.85	13.05	102.90	0	0	0
14	485	100:0	93.42	9.77	103.1	0	0	0
15	485	100:0	97.88	5.59	103.47	0	0	0
16	485	100:0	99.08	3.05	102.13	1.08	0	1.08
		Av. total Al recovered			100.7			

RECOVERY OF ALUMINA FROM GEORGIA SHALE EXTRACT

The hydrochloric acid extract of Georgia shale had the following composition, per 10 cc. of solution:

	Gram		Gram
$AlCl_3$	0.6816	$CaCl_2$	0.0041
$FeCl_3$	0.3208	$MgCl_2$	0.1065
KCl	0.5274		

In each experiment 10 cc. of the solution were placed in a platinum boat, the solution was evaporated overnight at 65° to 75° C., the boat was then placed in the furnace at 100° to 110° C. and heated in the same manner as the mixtures of pure aluminum and ferric chlorides. The hydrochloric acid gas was passed at the rate of 300 cc. per minute. At the end of the heating the contents of the boat were washed with water into a beaker, and soluble and insoluble aluminum and iron, and also potassium chloride determined. Duplicate experiments were made for each temperature, and in every case the duplicates are in fairly good agreement. The results are shown in Table II and graphically in Figures 2 and 3. The experimental points on the graphs are averages of the duplicate experiments. At the highest temperature employed, 588° C., an almost complete separation of iron and aluminum takes place. At this temperature the yields of aluminum in the form of alumina are 99.81 and 95.40 per cent, and the amounts of insoluble iron in the form of ferric oxide are 1.71 and 0 per cent. Any ferric oxide mixed with the alumina, after the ferric chloride has been washed out with water, can be removed by washing the residue with dilute hydrochloric acid, as will be shown later. Most of the ferric chloride escaped from the boat in the temperature interval 400° to 500° C., as seen from Figure 2. Although potassium chloride has a very small vapor pressure at the temperatures employed [according to Morgan (*9*), it is 1.54 mm. at 801° C.], a good deal of it, 40 to 48 per cent at 588° C., has left the boat together with the ferric chloride.

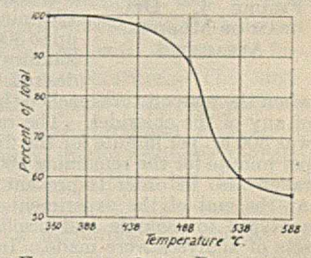


FIGURE 3. POTASSIUM CHLORIDE IN RESIDUE OF GEORGIA SHALE EXTRACT

TABLE II. POTASH, ALUMINUM, AND IRON IN THE RESIDUE OF GEORGIA SHALE EXTRACT

		Aluminum			Iron			
Expt.	Temp.	Insol.	Sol.	Total	Insol.	Sol.	Total	KCl
	° C.	%	%	%	%	%	%	%
17	350	66.54	32.22	98.76	16.06	83.13	99.19	100.00
18	350	65.27	28.77	94.04	19.44	75.60	95.04	100.00
19	438	81.81	20.17	101.98	13.22	66.40	79.62	99.05
20	438	79.55	18.45	98.00	9.99	65.34	75.23	96.15
21	488	85.42	6.02	91.44	6.89	17.27	24.16	86.75
22	488	81.05	6.82	87.90	5.20	21.19	26.39	90.35
23	538	85.20	6.06	91.26	6.08	5.13	11.21	63.85
24	538	91.86	4.84	96.70	4.86	2.16	7.02	56.65
25	588	99.81	0.03	99.84	1.71	0.28	1.99	51.80
26	588	95.40	1.05	96.45	0	0.81	0.81	60.00

The escape of the potassium chloride is probably due to the formation of a double salt, potassium-iron chloride (*10*). The curve for total aluminum recovered (Figure 2) has a depression between 450° and 550° C., indicating that some of the aluminum escaped from the boat. In view of the fact that, when pure mixtures of aluminum and ferric chlorides were heated, the total for soluble and insoluble aluminum added up, on the average, to about 100 per cent, it would seem that the escape of some of the aluminum from the boat might be due to the presence of potassium chloride, with which the aluminum chloride has a tendency to form double salts (*1*).

SEPARATION OF ALUMINA FROM GEORGIA SHALE EXTRACT WITHOUT VOLATILIZATION OF FERRIC AND POTASSIUM CHLORIDES

In this series of experiments the Georgia shale extract was evaporated to dryness by heating for several hours in an atmosphere of hydrochloric acid gas, up to 250° C. The resulting material was yellow, crystalline, and hygroscopic. Experiments with this crude salt were carried out in a modified apparatus shown in Figure 4.

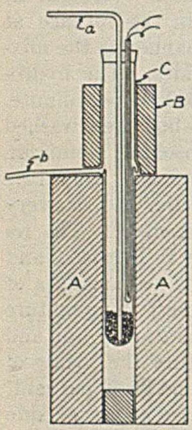


FIGURE 4. DIAGRAM OF MODIFIED APPARATUS

A glass tube, *C*, sealed at the bottom, was placed in a nichrome furnace, *A*. The crude salt was placed in this tube. Hydrochloric acid gas was led into the tube through *a* and out through *b*. A small nichrome furnace surrounded *C* above the side tube *b*. This furnace was kept at about 200° C. and served to prevent water from condensing on the inside of *C* and running back into the salt. The water vapor escaped together with the hydrochloric acid gas through *b*. A platinum–platinum rhodium thermocouple inserted in a glass tube served for temperature measurement. In each case 20 grams of the crude salt were placed in the tube *C*, and the furnace was heated as follows: During the first 120 minutes it was heated in every case up to 300° C. During the remaining 120 minutes it was heated to the highest point desired. The heating was discontinued when the temperature reached this point, to prevent volatilization of any of the chlorides. The rate of flow of hydrogen chloride was 300 cc. per minute for the first 120 minutes, and 20 to 30 cc. per minute for the remaining 160 minutes. This precaution was taken also in order to prevent volatilization of the chlorides. At the end of the experiment the material was collected and analyzed for soluble and insoluble aluminum and iron. Two sets of analyses were made. In one set, 1 gram of material in each case was washed first with 10 cc. of 0.212 *N* hydrochloric acid and then several times with water. The solution and the insoluble residue were then analyzed for aluminum and iron. In the second set of analyses, 1 gram of material in each case was washed several times with water, and the residue and solution were analyzed for aluminum and iron. The results are shown in Table III and Figure 5, and are given in per cent of amounts present in the crude salt extract. It is evident that by heating the Georgia shale extract to 588° C. and washing the residue with hydrochloric acid solution, pure alumina representing a 93 to 94 per cent yield can be obtained. The potassium chloride in this case will be in solution together with the ferric, calcium, and magnesium chlorides.

TABLE III. ALUMINUM AND IRON IN GEORGIA SHALE EXTRACT

EXPT.	TEMP.	ALUMINUM Insol.	ALUMINUM Sol.	IRON Insol.	IRON Sol.
	° *C.*	%	%	%	%
RESIDUE WASHED WITH 10 CC. 0.212 NORMAL HYDROCHLORIC ACID					
27	338	61.55	38.45	7.38	92.62
28	388	69.61	30.39	9.43	90.57
29	438	79.72	20.28	2.20	97.80
30	488	82.15	17.85	2.15	97.85
31	538	88.23	11.77	0	100
32	588	93.89	6.11	0	100
33	588	92.89	7.11	0	100
RESIDUE WASHED WITH WATER					
27	338	76.83	23.17	8.35	91.65
28	388	83.64	16.36	14.99	85.01
29	438	88.00	12.00	13.87	86.13
30	488	91.25	8.75	14.11	85.89
31	538	94.16	5.84	14.74	85.26
32	588	98.03	1.97	14.07	85.93
33	588	97.77	2.23	10.73	89.27

EFFECT OF AIR MIXED WITH HYDROCHLORIC ACID GAS ON HYDROLYSIS OF ALUMINUM AND FERRIC CHLORIDES

When mixtures of pure aluminum and ferric chlorides were heated, it was found that an atmosphere of air and hydrochloric acid gas, in the ratio of 50:50, gave as good results as 100 per cent hydrochloric acid. However, in the case of Georgia shale extract the results were different as shown conclusively in Table IV. Experiment 33 was described above and experiment 34 was made under similar conditions, except that the atmosphere consisted of air and hydrochloric acid in the ratio of 50:50. Rate of flow of gas mixture was the same here as in experiment 33. The presence of air caused decomposition of ferric chloride to ferric oxide, which could not be washed out even with dilute hydrochloric acid.

TABLE IV. EFFECT OF AIR ON HYDROLYSIS OF ALUMINUM AND IRON CHLORIDES

EXPT.	RATIO HCl:AIR	WASHED IN:	ALUMINUM Insol.	ALUMINUM Sol.	IRON Insol.	IRON Sol.
			%	%	%	%
33	100:0	H_2O	97.77	2.23	10.73	89.27
34	50:50	H_2O	97.27	2.73	26.05	73.95
33	100:50	HCl	92.89	7.11	0	100
34	50:50	HCl	94.93	3.07	12.30	87.70

CONCLUSION

On the basis of the data presented, it may be concluded that a separation of alumina in pure form from the hydrochloric acid extract of Georgia shale can be effected by heating to about 600° C. in the presence of hydrochloric acid gas, whereby, of all the chlorides present in that system, the aluminum chloride alone is converted to the insoluble oxide. By modifying conditions, the ferric chloride may be volatilized or by an alternative procedure may be quantitatively separated from the alumina by leaching. Of all the chlorides in solution from the leaching, potassium chloride is the only one not readily converted to the oxide by heating in an atmosphere of steam. This provides a means of separating the potash as high-grade potassium chloride with the recovery of hydrochloric acid from the other salts.

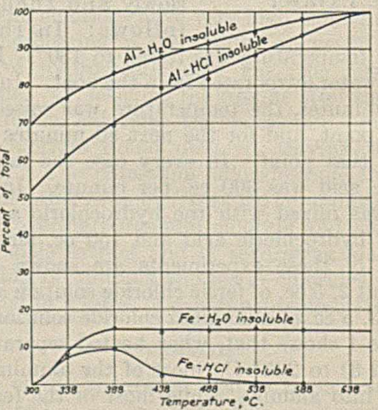


FIGURE 5. ALUMINUM AND IRON INSOLUBLE IN WATER AND HYDROCHLORIC ACID

ACKNOWLEDGMENT

The writer wishes to acknowledge his indebtedness to J. W. Turrentine for the interest which he has taken in this work and for many valuable suggestions.

LITERATURE CITED

(1) Baud, *Ann. chim. phys.*, [8] 1, 8 (1904).
(2) Doremus, *J. Soc. Chem. Ind.*, 36, 1094 (1917).

(3) Dumas, *Ann. chim. phys.*, [3] 55, 187 (1859).
(4) Gooch and McClenahan, *Am. J. Sci.*, [4] 17, 365 (1904).
(5) Hempel, *Ber.*, 21, 897 (1888).
(6) Hulin, French Patent 23,828 (1917).
(7) Madorsky, Ind. Eng. Chem., 24, 233 (1932).
(8) Meier, Bur. Mines, *Tech. Paper* 360, 40 (1925).
(9) Morgan, Dissertation, Columbia University, 1919.
(10) Neumann, *Ber.*, 18, 2890 (1885).
(11) Ralston, Bur. Mines, *Tech. Paper* 321, 34 (1923).
(12) Reed, Fox, and Turrentine, Ind. Eng. Chem., 24, 910 (1932).
(13) Richards, *J. Am. Chem. Soc.*, 24, 374 (1903).
(14) Sainte-Claire-Deville, *Ann.*, 120, 180 (1861).

Received September 20, 1933. Presented before the Division of Fertilizer Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.

Thermal Decomposition of Hydrocarbons and Engine Detonation

F. O. Rice, Johns Hopkins University, Baltimore, Md.

The thermal decomposition of the fuel probably plays an appreciable role in the reactions occurring in the internal combustion engine. This decomposition results in one molecule of the fuel being replaced by several molecules; this increase in concentration may greatly augment the rate of oxidation. Different hydrocarbons yield different numbers of molecules of products per mole decomposed, and calculation shows a strict parallelism between this and the knocking tendency. The knocking tendency increases with increase of number of moles of product per mole decomposed. One effect of antiknock compounds is to reduce the number of moles of products formed from the decomposition of one mole of hydrocarbon.

A SURVEY of the literature (*12*) on the subject of explosions and flames shows that the first step in such reactions is usually followed by an extremely complex series of reactions; the view is widely held that many of these subsequent reactions are of the chain type since on this basis many of the peculiarities of explosions, such as sensitivity to small traces of impurities and the existence of fairly sharply defined limits of pressure and temperature, can be explained. Further evidence to this effect (*4*) seems to be found in the fact that these reactions are sometimes stopped by surfaces, sometimes start at surfaces, and sometimes are both stopped and started at a surface. Experimental work on the oxidation of gaseous paraffin hydrocarbons has shown (*2, 9*) that the oxidation results in a complex series of intermediate oxidation products; the oxidation processes which occur in the internal combustion engine must, therefore, be extremely complex, and it is hardly possible to offer more than the most general interpretation of the course of the reaction.

However, it has occurred to the author that in the case of hydrocarbon-oxygen mixtures, a preliminary decomposition of the hydrocarbon into lower hydrocarbons, chiefly the lower olefins and paraffins, resulting partly from the purely thermal effect and partly from attack on the hydrocarbon by molecular fragments, probably takes place.

If this preliminary decomposition were extensive, the chemical composition of the mixture after the decomposition but before appreciable oxidation had set in would be approximately the same for all hydrocarbons; the only substantial difference would be in the number of smaller hydrocarbons produced per molecule of the original fuel. Since the concentration of the total hydrocarbon molecules probably plays a considerable role in determining the pressure of the hydrocarbon-oxygen mixture at which detonation sets in, it seemed worth while to calculate the products formed in the thermal decomposition of different hydrocarbons and to attempt to correlate the results with measurements of the knocking tendencies of different hydrocarbons.

There is considerable evidence both from the experimental and from the theoretical standpoint that the simple thermal decomposition of hydrocarbons plays an appreciable part in the processes occurring during their oxidation (*13*). For example, experimental evidence is given in a paper by Pease (*8*) on the oxidation of propane and butane. The nonexplosive oxidation of these compounds at temperatures far below those required to produce appreciable cracking of the hydrocarbons in the absence of oxygen yielded considerable quantities of hydrogen, methane, and unsaturated hydrocarbons, the amounts increasing with increasing furnace temperature. The similarity between the composition of these products and those formed in the ordinary thermal decomposition led Pease to suggest that the oxidation of hydrocarbons was accompanied to a greater or less degree by a decomposition similar to that occurring in the absence of oxygen. The theoretical evidence which will be discussed in detail later supports the view that, even in homogeneous hydrocarbon-oxygen mixtures, thermal decomposition accompanies the oxidation of the hydrocarbon to a considerable extent.

The lack of homogeneity of the gases which enter the cylinder of an internal combustion engine will naturally favor still more the thermal decomposition of the hydrocarbon molecule. Even under the best conditions—namely, when all the fuel is volatilized before entering the cylinder and turbulence is induced in the gaseous mixture—the mixing of air and hydrocarbon vapor must be far from perfect. When part of the fuel is not volatilized but enters the cylinder in the form of small droplets, we should expect to find many segregated volumes, each consisting mainly of hydrocarbon vapor. During the compression stroke and in the earlier stages of the explosion these segregated volumes may be expected to undergo ordinary thermal decomposition into simpler products, independently of the decomposition induced by the oxidation reactions.

If thermal decomposition does occur to any appreciable extent, it must have considerable bearing on the detonation of hydrocarbon-oxygen mixtures since through this decomposition process one molecule of hydrocarbon is suddenly replaced by several smaller molecules. The effect of this is twofold: (1) Since the pressure exerted by a gas depends on the number of molecules and not on their size, this process is equivalent to raising the compression in the engine from 5 to

TABLE I. THERMAL DECOMPOSITION OF HYDROCARBONS

(Methyl, ethyl, isopropyl, and *tert*-butyl radicals assumed to be stable; relative chances of loss of primary, secondary, and tertiary hydrogen atoms assumed to be 1:2:10, respectively)

Hydrocarbon	Moles Product per Mole Hydrocarbon	Aniline Ratio (*6*)
N-pentane	2.34	1
2-Methylbutane	2.0	9
2,2-Dimethylpropane	2.0	15
N-hexane	2.64	−6
2-Methylpentane	2.22	4
3-Methylpentane	2.22	8
2,2-Dimethylbutane	2.0	13
2,3-Dimethylbutane	2.0	19
N-heptane	2.94	−14
2-Methylhexane	2.65	0
3-Methylhexane	2.44	3
3-Ethylpentane	2.3	4
2,2-Dimethylpentane	2.38	8
2,4-Dimethylpentane	2.17	8
2,3-Dimethylpentane	2.17	12
3,3-Dimethylpentane	2.3	13
2,2,3-Trimethylbutane	2.0	19
N-decane	3.74	−30
2,7-Dimethyloctane	3.26	−10
3,3,4,4-Tetramethylhexane	2.62	..
3,4-Dimethyloctane	2.42	..
2,2,6,6-Tetramethylhexane	2.35	29
N-octane	3.2	−21
3-Methylheptane	2.97	..
2-Methylheptane	2.95	..
4-Methylheptane	2.77	..
2,2-Dimethylhexane	2.65	..
2,5-Dimethylhexane	2.65	5
3,3-Dimethylhexane	2.63	..
3-Ethylhexane	2.49	..
2,4-Dimethylhexane	2.49	..
2,3-Dimethylhexane	2.41	..
3-Methyl-3-ethylpentane	2.38	..
3,4-Dimethylhexane	2.33	..
2,2,4-Trimethylpentane	2.26	16
2,2,3-Trimethylpentane	2.26	17
2-Methyl-3-ethylpentane	2.23	..
2,3,3-Trimethylpentane	2.21	..
2,3,4-Trimethylpentane	2.14	..
2,2,3,3-Tetramethylbutane	2.0	26
N-Nonane	3.48	−28
2,6-Dimethylheptane	2.82	− 6
4-Ethylheptane	2.58	..
3,3-Diethylpentane	2.43	..
3-Methyl-4-ethylhexane	2.36	..
2,4-Dimethyl-3-ethylpentane	2.18	..
2,3,3,4-Tetramethylpentane	2.16	..

25 per cent, depending on the fuel used and the richness of the mixture entering the cylinder. This effect is therefore comparatively small and in comparison with the second effect may be neglected; (2) since the rate of oxidation of the fuel is very sensitive to the number of fuel molecules per unit volume, decomposition of these molecules will obviously increase the rate of oxidation, possibly to a very great extent. In this connection, Thompson and Hinselwood (*14*) showed that the rate of oxidation of ethylene is proportional to the third power of the ethylene concentration. If this law holds under the conditions in the cylinder, the decomposition of a long chain hydrocarbon into ethylene molecules may increase the rate of oxidation by several orders.

Since different hydrocarbons yield different numbers of molecules of product per molecule decomposed, it seemed of interest to calculate these numbers and compare them with the experimentally determined knocking tendency of hydrocarbons. It is clear that on the basis of our premise we would expect the knocking tendency to increase with an increasing number of molecules of product formed per molecule of hydrocarbon thermally decomposed.

METHOD OF CALCULATION

Precise experimental measurements of the products of decomposition of the saturated hydrocarbons up to and including the pentanes and two of the hexanes are now available (*3*), but there do not seem to be any such data for the higher hydrocarbons. It is, however, possible to calculate the products to be expected on the basis of a theory recently proposed (*10*). This theory postulates that the decomposition of hydrocarbons proceeds through a mechanism involving the production of free radicals and the subsequent removal of hydrogen atoms from the surrounding hydrocarbon molecules by reaction with these radicals. If, for example, we consider butane, the removal of a hydrogen atom must leave either a *N*-butyl or an isobutyl radical. From the pentanes and higher hydrocarbons a greater variety of radicals will be obtained, depending on the number of different kinds of hydrogen atoms in the molecule. Most of these larger radicals are very unstable and rapidly decompose into olefins and smaller radicals. We may expect that substantially this same process occurs, at least to some degree, in the oxidation of hydrocarbons, except that a hydrogen atom may now be picked off from the hydrocarbon molecule by reaction with an oxygen molecule as well as with a molecular fragment produced in one of the steps occurring in the oxidation processes. The free radical produced by removal of a hydrogen atom from a hydrocarbon molecule may now either decompose into olefins and a smaller free radical, or it may react with oxygen to give an aldehyde in some such way as suggested by Bates and Spence (*1*). In general we can state that the large radicals are unstable (i. e., their decomposition has a low energy of activation) and so the unimolecular decomposition will be favored as opposed to the bimolecular oxidation process. However the work of Pope, Dykstra, and Edgar (*9*) shows that under certain conditions there is considerable aldehyde formation in the oxidation of the octanes.

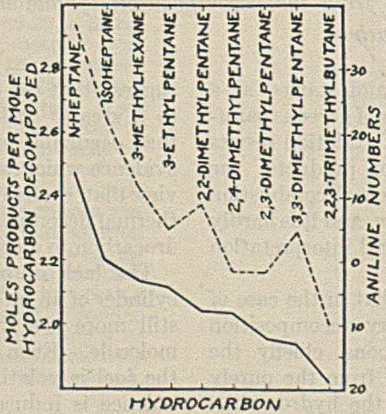


FIGURE 1. COMPARISON OF THERMAL DECOMPOSITION OF HYDROCARBONS (DOTTED CURVE) AND KNOCKING TENDENCY (FULL CURVE)

In the following calculations of the decomposition products of hydrocarbons the method described in previous publications (*11*) has been followed exactly, with one exception: it has been assumed that in addition to the methyl and ethyl radicals, the isopropyl and *tert*-butyl radicals are also stable. This assumption is justified because: (1) the decomposition in the cylinder must always occur under considerable pressure, and this favors the reaction of the radicals with surrounding molecules rather than their decomposition; and (2) these four radicals may be expected to have a higher degree of stability than any other alkyl radicals because their decomposition can occur only through the breaking off of atomic hydrogen.

It is not necessary to give all these calculations in detail because the method has already been fully described and applies to all the paraffin hydrocarbons. Consequently, the method will be illustrated in detail with reference to only two hydrocarbons, *N*-octane and 2, 2, 4-trimethylpentane. Furthermore only the chain cycles will be given since these determine the products of the decomposition (R represents a free alkyl radical or a hydrogen atom):

N-octane: $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

$$\begin{aligned}
A_1\text{: } C_8H_{18} + R &\longrightarrow RH + CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2—\\
&\longrightarrow RH + C_2H_4 + CH_3CH_2CH_2CH_2CH_2CH_2—\\
&\longrightarrow RH + 2C_2H_4 + CH_3CH_2CH_2CH_2—\\
&\longrightarrow RH + 3C_2H_4 + CH_3CH_2—
\end{aligned}$$

$$\begin{aligned}
A_2\text{: } C_8H_{18} + R &\longrightarrow + CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH(CH_3)—\\
&\longrightarrow RH + C_3H_6 + CH_3CH_2CH_2CH_2CH_2—\\
&\longrightarrow RH + C_3H_6 + C_2H_4 + CH_3CH_2CH_2—\\
&\longrightarrow RH + C_3H_6 + 2C_2H_4 + CH_3—
\end{aligned}$$

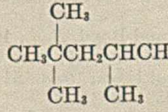
$$\begin{aligned}
A_3\text{: } C_8H_{18} + R &\longrightarrow RH + CH_3CH_2CH_2CH_2CH_2CH_2CH\text{-}(CH_2CH_3)—\\
&\longrightarrow RH + CH_3CH_2CH_2CH_2CH_2CH_2CH{:}CH_2 + CH_3—\\
\text{or } &\longrightarrow RH + CH_3CH_2CH{:}CH_2 + CH_2CH_2CH_2\text{-}CH_2—\\
&\longrightarrow RH + CH_3CH_2CH{:}CH_2 + C_2H_4 + CH_3CH_2—
\end{aligned}$$

$$\begin{aligned}
A_4\text{: } C_8H_{18} + R &\longrightarrow RH + CH_3CH_2CH_2CH_2CH_2CH\text{-}(CH_2CH_2CH_3)—\\
&\longrightarrow RH + CH_3CH_2CH_2CH_2CH{:}CH_2 + CH_3CH_2—\\
\text{or } &\longrightarrow RH + CH_3CH_2CH_2CH{:}CH_2 + CH_3CH_2CH_2—\\
&\longrightarrow RH + CH_3CH_2CH_2CH{:}CH_2 + C_2H_4 + CH_3—
\end{aligned}$$

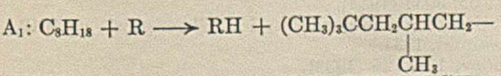
The following is a summary of the decomposition in which the two alternative methods of decomposition in the chains A_3 and A_4 have been given equal weight; the ratio 1:2:10 has been adopted for the relative chance of reaction of a primary, secondary, and tertiary hydrogen atom, respectively. This ratio corresponds to 600° C. and would have to be diminished slightly if the decomposition in the cylinder occurred at a higher temperature:

$$\begin{aligned}
A_1\text{: } 6C_8H_{18} &\longrightarrow 6C_2H_6 + 18C_2H_4\\
A_2\text{: } 8C_8H_{18} &\longrightarrow 8CH_4 + 16C_2H_4 + 8C_3H_6\\
A_3\text{: } 8C_8H_{18} &\longrightarrow 4CH_4 + 4C_7H_{14}(N) + 4C_2H_6 + 4C_2H_4 + 4C_4H_6(N)\\
A_4\text{: } 8C_8H_{18} &\longrightarrow 4C_2H_6 + 4C_6H_{12}(N) + 4CH_4 + 4C_2H_4 + 4C_5H_{10}(N)
\end{aligned}$$

Thus *N*-octane decomposes according to four cycles; one molecule of *N*-octane produces either 4 or 2.5 molecules, according to whether cycles A_1 or A_2, or cycles A_3 or A_4 are followed, respectively; the weighted mean of all the methods of decomposition is 3.2. There is, therefore, a considerable increase in the number of molecules present when *N*-octane decomposes thermally:

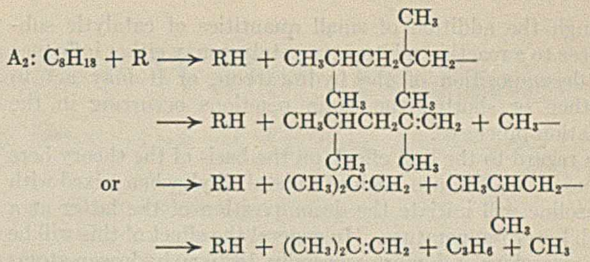
2,2,4-Trimethylpentane: 

$$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\underset{CH_3}{CH}CH_3$$



$$A_1\text{: } C_8H_{18} + R \longrightarrow RH + (CH_3)_3CCH_2\underset{CH_3}{CH}CH_2—$$

$$\begin{aligned}
&\longrightarrow RH + (CH_3)_3CCH_2CH{:}CH_2 + CH_3—\\
\text{or } &\longrightarrow RH + C_3H_6 + (CH_3)_3CCH_2—\\
&\longrightarrow RH + C_3H_6 + (CH_3)_2C{:}CH_2 + CH_3—
\end{aligned}$$



$$\begin{aligned}
A_2\text{: } C_8H_{18} + R &\longrightarrow RH + CH_3\underset{CH_3}{CH}CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2—\\
&\longrightarrow RH + CH_3\underset{CH_3}{CH}CH_2\underset{CH_3}{C}{:}CH_2 + CH_3—\\
\text{or } &\longrightarrow RH + (CH_3)_2C{:}CH_2 + CH_3\underset{CH_3}{CH}CH_2—\\
&\longrightarrow RH + (CH_3)_2C{:}CH_2 + C_3H_6 + CH_3
\end{aligned}$$

$$\begin{aligned}
A_3\text{: } C_8H_{18} + R &\longrightarrow RH + (CH_3)_3CCH[CH(CH_3)_2]—\\
&\longrightarrow RH + (CH_3)_3CCH{:}CHCH_3 + CH_3—\\
\text{or } &\longrightarrow RH + (CH_3)_2C{:}CHCH(CH_3)_2 + CH_3—\\
A_4\text{: } C_8H_{18} + R &\longrightarrow RH + (CH_3)_3CCH_2\ C[(CH_3)_2]—\\
&\longrightarrow RH + (CH_3)_2C{:}CH_2 + (CH_3)_2C—
\end{aligned}$$

Summarizing as before we obtain:

$$\begin{aligned}
A_1\text{: } 6C_8H_{18} &\longrightarrow 3CH_4 + 3(CH_3)_3CCH_2CH{:}CH_2 + 3CH_4 + 3C_3H_6 + 3C_4H_8(\text{iso})\\
A_2\text{: } 9C_8H_{18} &\longrightarrow 4.5CH_4 + 4.5(CH_3)_2CHCH_2C{:}CH_3CH_2 + 4.5CH_4 + 4.5C_3H_6 + 4.5C_4H_{10}(\text{iso})\\
A_3\text{: } 4C_8H_{18} &\longrightarrow 2CH_4 + 2(CH_3)_3CCH{:}CHCH_3 + 2CH_4 + 2(CH_3)_2C{:}CHCH(CH_3)_2\\
A_4\text{: } 10C_8H_{18} &\longrightarrow 10C_4H_{10}(\text{iso}) + 10C_4H_8(\text{iso})
\end{aligned}$$

Thus octane also decomposes according to four methods, but in this case one molecule yields only 2.5, 2.5, 2, and 2 molecules of products, respectively; the weighted mean of these is 2.26 so that the expansion of this hydrocarbon is decidedly less than *N*-octane on thermal decomposition; the knocking tendency has also been found to be less, which is in agreement with the theory.

The final results of these calculations are given in Table I. To obtain these results it is not necessary to work out each hydrocarbon in the detailed way given for *N*-octane and 2,2,4-trimethylpentane; after some practice it is possible to summarize the different chain reactions by inspection and obtain the final result readily. Table I also includes the aniline numbers of Lovell, Campbell, and Boyd (*6*) whenever these were available. Figure 1 shows a comparison of the calculated values for the heptanes with their experimentally determined antiknock values. The parallelism between the calculated and experimental results suggests that the thermal decomposition of hydrocarbon molecules is one of the contributing factors in engine detonation.

It should be possible to submit this theory to experimental test by withdrawing samples of the reaction mixture from the cylinder in the early stages of the combustion by some such method as that used by Lovell, Coleman, and Boyd (*7*). The products to be expected from the thermal decomposition of several paraffin hydrocarbons are given in Table II; on the basis of the present theory these products should be formed either before or just after the mixture is sparked.

ACTION OF ANTIKNOCK COMPOUNDS

In considering any theory of antiknock action, we must distinguish carefully between two effects which can arise

TABLE II. MOLES OF PRODUCTS FORMED PER MOLE OF HYDROCARBON THERMALLY DECOMPOSED

(Methyl, ethyl, isopropyl, and *tert*-butyl radicals assumed to be stable; relative chances of loss of primary, secondary, and tertiary hydrogen atoms assumed to be 1:2:10, respectively; these products should be formed in the ordinary thermal decomposition of hydrocarbons at 600° C. and under pressure.)

HYDROCARBON	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	*N*-C_4H_8	*sec*-C_4H_8	Iso-C_4H_8	Iso-C_4H_{10}	HIGHER OLEFINS
N-hexane	0.546	0.91	0.455	0.364	...	0.182	...	...	...	0.182
3-Methylpentane	0.74	0.223	0.26	0.223	...	0.111	0.148	...	...	0.52
2,3-Dimethylbutane	0.81	...	...	0.188	0.188	...	...	...	...	0.81
N-heptane	0.54	1.17	0.463	0.308	...	0.154	...	...	...	0.308
2,4-Dimethylpentane	0.445	...	...	0.334	0.0556	...	...	0.556	...	0.278
2,2,3-Trimethylbutane	0.7	...	...	0.12	0.18	...	...	0.18	0.18	0.7
N-octane	0.534	1.4	0.467	0.267	...	0.133	...	...	...	0.4
2,5-Dimethylhexane	0.75	0.15	...	0.15	0.75	...	...	0.5	...	0.35
2,2,4-Trimethylpentane	0.656	...	...	0.259	...	...	...	0.605	0.346	0.397
N-nonane	0.53	1.65	0.471	0.236	0.118	...	...	...	...	0.471
2,6-Dimethylheptane	0.455	0.591	...	0.364	0.546	...	...	0.455	...	0.41
N-decane	0.528	1.9	0.474	0.211	...	0.105	...	...	...	0.526
2,2,6,6-Trimethylhexane	0.5	0.347	...	...	...	...	...	0.347	0.5	0.654

through the addition of small quantities of catalytic substances to a reaction mixture; a catalyst may either influence the decomposition of the hydrocarbon, or it may act to lengthen or shorten the chain reactions occurring in the oxidation processes.

In regard to the first effect, on the basis of the theory here proposed, a substance, such as a metal alkyl, when mixed with a gasoline will initiate the decomposition of the latter at a much lower temperature. In general the effect of this will be that secondary and, more especially, tertiary hydrogen atoms will react relatively much more easily than the more strongly bound primary hydrogen atoms, and the lower the temperature of decomposition the more marked will be this effect. In general the result will be fewer molecules of products per molecule of hydrocarbon decomposed, and consequently less knocking. In view of our lack of knowledge of the binding strengths of different carbon-hydrogen bonds it is not desirable to attempt to make detailed calculations. However, even without precise calculations we obtain the surprising result that hydrocarbons, such as 2,5-dimethylhexane or 2,6-dimethylheptane which have tertiary hydrogen atoms near the end of the chain, should yield more molecules when decomposed in the presence of a catalyst such as tetraethyllead than in its absence; for such hydrocarbons, therefore, tetraethyllead should act as a knock inducer in so far as it affects the thermal decomposition of the hydrocarbon.

The chief requirement of an efficient antiknock compound lies in its ability to produce free radicals at a temperature such that these can initiate chains and thus promote the decomposition of the hydrocarbon. If the catalyst decomposes at too low a temperature, the free radicals will recombine with each other; if decomposition takes place at too high a temperature, the compound will lose in efficiency through the fact that the chains involving primary hydrogen atoms will increase in relation to those involving secondary and tertiary hydrogen atoms, since the latter predominate more and more, the lower the temperature. The actual measure of this effect is determined by the activation energy of the decomposition of the antiknock compound. On the basis of this theory a great many of the compounds suggested as catalysts to lessen detonation cannot have any value because the activation energy of the decomposition reaction is far too high. Judging from empirical experimental evidence, it would seem that an activation energy between 30,000 and 40,000 calories is required for efficiency; of the compounds mentioned in this capacity in the literature (*5*) only certain of the metal alkyls meet the requirements.

A further experimental test is possible through a comparison of the results of two experiments, in one of which a given concentration of an antiknock substance such as tetraethyllead is dissolved in the gasoline, and in the other of which the tetraethyllead is vaporized at the air intake in such amount that its concentration in the cylinder is approximately the same as in the first experiment. All the other factors in both experiments must of course be kept as nearly identical as possible. If the tetraethyllead really acts as a catalyst by inducing the thermal decomposition of the hydrocarbon at a lower temperature than would otherwise be the case, it should be more efficient in the first experiment, where it is mixed directly with the hydrocarbon, than in the second, where it is first mixed with air.

There is the further possibility that some substances may exist which stabilize paraffin hydrocarbons by terminating the chains of their thermal decomposition. The effect of such a substance would be to raise the temperature at which the hydrocarbon decomposes and in this way to favor, relatively, the reaction chains involving primary hydrogen atoms, thus causing an increase in the number of molecules of products per molecule of hydrocarbon, and therefore increasing the tendency towards knocking. No substances which diminish the rate of thermal decomposition of hydrocarbons have so far been reported, but, in view of the property of some organic nitrites of inducing knocking, it would seem desirable to test this class of compounds for this effect.

So far only the possible effect of catalysts on the ordinary thermal decomposition of the fuel has been discussed. There is, however, a second effect that the catalyst may have by affecting the chain reactions that constitute the oxidation processes. The most characteristic property of these oxidation chains is their sharply defined critical limit of pressure and of temperature, at which the rate of the oxidation suddenly changes from a very slow reaction to a violent detonation. It seems entirely possible that catalysts introduced into the cylinder may suppress or accelerate knocking by their effect on these oxidation chains. Since such oxidation chains are usually very sensitive to the effect of surface, it is quite conceivable that lead or tellurium dust formed by the thermal decomposition of the alkyls may favor destruction of the oxidation chains and thus diminish the violence of the explosion. This hypothesis could be tested by comparing the effect of tetraethyllead with that of another compound, the thermal decomposition of which has the same activation energy but does not produce a nonvolatile dust.

LITERATURE CITED

(1) Bates and Spence, *J. Am. Chem. Soc.*, **53**, 1689 (1931).
(2) Egloff and Schaad, *Chem. Rev.*, **6**, 91 (1929).
(3) Frey and Hepp, IND. ENG. CHEM., **25**, 441 (1933).
(4) Hinselwood, *Trans. Faraday Soc.*, **28**, 184 (1932).
(5) Kalichevsky and Stagner, "Chemical Refining of Petroleum," p. 281, A. C. S. Monograph No. 63, Chemical Catalog Co., 1933.
(6) Lovell, Campbell, and Boyd, IND. ENG. CHEM., **23**, 26, 555 (1931).
(7) Lovell, Coleman, and Boyd, *Ibid.*, **19**, 373 (1927).
(8) Pease, *J. Am. Chem. Soc.*, **51**, 1839 (1929).
(9) Pope, Dykstra, and Edgar, *Ibid.*, **51**, 2203 (1929).
(10) Rice, *Ibid.*, **53**, 1959 (1931).
(11) Rice, *Ibid.*, **55**, 3035 (1933).
(12) Rice and Urey, "Treatise on Physical Chemistry," p. 1012, Van Nostrand, 1931.
(13) Steele, *Nature*, **131**, 725 (1933).
(14) Thompson and Hinselwood, *Proc. Roy. Soc.* (London), **A125**, 277 (1929).

RECEIVED September 22, 1933.

USE OF WOOL FOUND NOT FEASIBLE IN ROAD CONSTRUCTION. Experiments with wool as a material for road construction conducted in Australia have not proved successful, according to a consular report from Melbourne, made public by the Commerce Department.

The experiments were undertaken as a result of reports that graziers had been making use of low-grade wool for the improvement of private roads on their properties. The Department of Roads of New South Wales constructed a short trial section of road in a district where the soil was typical of that of the country roads in the state. It was found that the wool used as a binder for pavement provided a good running surface when the road was dry and beaten down by traffic, but that in wet weather it collected on the wheels of vehicles and made progress extremely difficult.

The experiment has now had nine months of trial and the conclusions are that the wool does not impregnate the soil to any extent but rather tends to work through and disassociate itself from the soil in dry periods. Reënforcement of the soil has not been apparent. It is probable, as a result of the experiments, that the Department of Roads will abandon any further attempts to employ wool in road construction, the report declares.

Solid Matter in Boiler-Water Foaming

II. Loss of Foam-Stabilizing Properties at Higher Pressures

C. W. Foulk and S. F. Whirl, Ohio State University, Columbus, Ohio

Various kinds of finely divided solid matter lost their foam-stabilizing properties in 5 to 10 minutes in a dilute salt solution (synthetic boiler water) at pressures of 7.0 to 10.6 kg. per sq. cm. (100 to 150 pounds per square inch). The rate of loss increases with the pressure (temperature) of the solution.

Solids that have lost their foam-stabilizing effects not only no longer promote foaming and priming in a boiler but actually reduce it because of the greater smoothness of boiling induced. The work of Joseph and Hancock on the effect of solids on priming was repeated and their results were confirmed, if the experiments were made in the same way, but their generalization that solids have no effect on priming is hardly warranted.

THE experiments of this paper had two objectives: first, to test the hypothesis advanced by Foulk and Hansley (*2*) that certain kinds of solid matter rapidly lose their foam-stabilizing properties at the high temperature of a steam boiler, and secondly, to see what bearing this hypothesis, if found true, would have on the conclusions of Joseph and Hancock (*3*)—namely, that solid matter in a boiler has no effect on the throw-over of water into the steam. With this second objective in view, an experimental boiler was built like the one employed by Joseph and Hancock. It also served for testing the hypothesis of Foulk and Hansley.

Experimental Boiler

The boiler is shown with its essential details and dimensions in Figures 1, 2, and 3. The glass windows are flat glass water-level gages. With a light at the end of the boiler opposite the observer, the appearance of both steam and water could be followed.

The so-called charging cylinder, Figure 2 (an appliance not used by Joseph and Hancock), served for the addition of solid matter after working pressure had been reached in the boiler. Its operation was as follows:

With all valves closed excepting the top one, the finely ground material mixed with a little water was placed in the cylinder. The top valve was then closed and the one on the by-pass opened. In this way the pressure in the charging cylinder was the same as that in the boiler; therefore, as soon as the desired boiler pressure was reached, opening the lower valve of the cylinder allowed the solid matter to drop at once into the salt solution in the boiler.

Two valves (*A* and *B*, Figure 2) were employed on the steam line, valve *A* serving as an adjustable standard orifice. The boiler charged with distilled water was heated to the desired pressure, and then, with both valves open, boiling was continued till the water level was lowered to the point at which priming[1] ceased, determined by observation through the glass windows. Valve *A* was then adjusted, valve *B* being wide open, so that the desired pressure would remain constant for 10 minutes, with rapid boiling and distillation going on. This setting of valve *A* was then retained for the entire series of runs made subsequently at that pressure. All that was necessary in starting a run was the rapid opening of *B* to its full extent. The agreement among runs made in this way was excellent when the nature of the experiments is considered. Figure 4 shows a graph of four runs, together with the average.

Experimental Procedures[2]

Two procedures were followed: (I) The cold boiler charged with salt solution or solution and solid matter was heated rapidly with valve *B* closed till the desired pressure was reached. Valve *B* was then opened and evaporation allowed to proceed to the end of the run.

(II) The second procedure was like the first except in the addition of solid matter. This was not done till the boiler had reached the desired pressure. Then, by means of the charging cylinder the solids were added and the run was immediately begun.

A run during which 6 liters of ejectate were collected lasted about 10 minutes.

Priming was measured chemically by titrating portions of the ejected boiler water and condensed steam with silver nitrate solution. Percentage priming means the percentage by volume of liquid boiler water in the portion of the ejectate examined. The total ejectate was passed through a large condenser, and the mixed water and condensed steam were collected in portions of 500 to 1000 cc. each. Since the total was condensed and examined, there was no question of sampling.

Water level in the boiler is indicated by the number of liters of solution. The water level fell steadily during a run, which accounts for the rapid drop in percentage of priming.

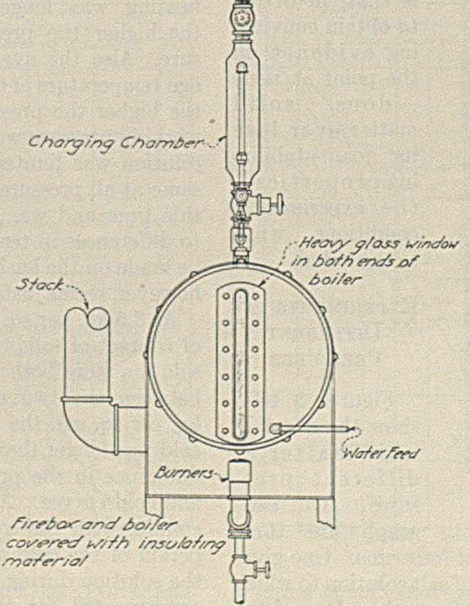


Figure 1. End View of Boiler

---

[1] The word priming as used in this paper means merely the passing of liquid water into the steam line.

[2] It is not clear in all cases in the paper by Joseph and Hancock (*3*) whether the salt solutions and solid matter used were placed in the cold boiler and heated to working pressure, or whether a part of the mixture was added (pumped into the boiler) after working pressure had been reached. Hancock has, however, kindly supplied the necessary details and an inspection of the data in the light of this added information shows as good agreement with the results of this paper as could be expected in view of the lower concentrations of salts and solid matter employed by Joseph and Hancock.

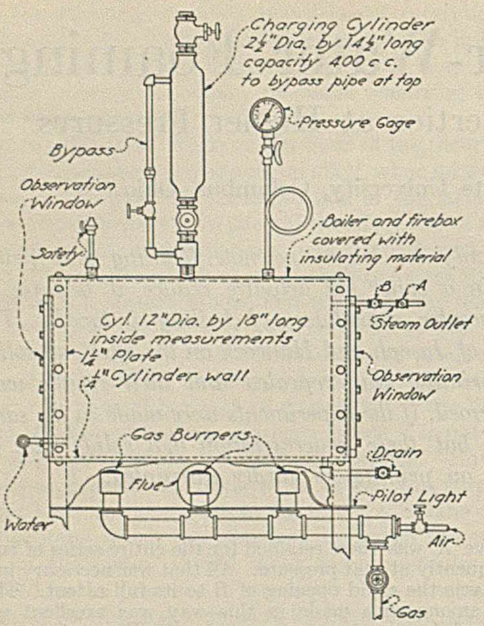


FIGURE 2. SIDE VIEW OF BOILER

Metric dimensions: 30.5 cm. diameter, 45.7 cm. long; end plates, 3.2 cm. thick; cylinder wall, 0.6 cm. thick; charging cylinder, 6.4 cm. diameter, 36.8 cm. long.

The solid matter used consisted of limestone, dolomite, ground flint, bituminous coal, galena, and boiler scale, all finely ground and passed through a 150-mesh sieve. This material was chosen because of the wide variety of foam-stabilizing properties presented.

For the synthetic boiler waters, sodium chloride solutions were used because they are of medium foaminess. In order to keep down corrosion, 50 p. p. m. of sodium hydroxide were added in all cases.

The authors wish to anticipate at this point the possible criticism that the materials and the concentrations employed were frequently out of accord with actual boiler practice. The reply is that, in order to obtain convincing evidence on the point at issue—does solid matter ever lose its foam-stabilizing properties—the experimental conditions were exaggerated.

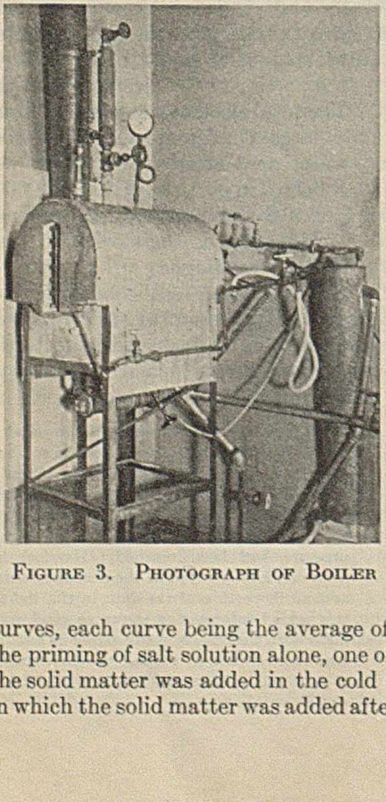


FIGURE 3. PHOTOGRAPH OF BOILER

EXPERIMENTS AT DIFFERENT PRESSURES

Figures 5 to 8 show the effect of solid matter at different pressures. On each graph are three curves, each curve being the average of four runs. One gives the priming of salt solution alone, one of salt solution to which the solid matter was added in the cold (procedure I), and one in which the solid matter was added after the working-pressure had been reached (procedure II). Powdered limestone was chosen as the solid matter because previous experiments had shown that the specimen at hand lost its foam-stabilizing properties relatively slowly.

A study of the curves shows that, as the pressure increases, the increase in priming caused by the solid matter decreases, till at 7 kg. per sq. cm. (100 pounds per square inch) and higher there is no significant difference between the priming of a salt solution alone and one with solids present. At the higher pressures, therefore, the results are in harmony with those of Joseph and Hancock. At low pressure, however, the solid matter greatly increased the priming, whereas these British investigators found little evidence of such an effect. These differences in results are not necessarily significant because they used different material and lower concentrations than those employed here.

On comparing the two ways of adding the solid matter, it is seen that at the lowest pressure there was no difference. At 5.3 kg. per sq. cm. (75 pounds per square inch), however, and during the earlier part of the runs at 7.0 and 10.6 kg. (100 and 150 pounds), the priming due to the solids added after working pressure was reached (procedure II) was greater than that of the solids added in the cold (procedure I).

Since the details of foaming and priming experiments are often determining factors, it is worth while to analyze the conditions with these two ways of adding solids to the boiler.

When the solids were added in the cold (procedure I), their contact with the solution was longer than in the case of procedure II, because they were in the boiler during the period of heating up to working pressure, and this period of heating was longer, the higher the pressure. Also the average temperature of the solution during this period was higher, the higher the pressure. When the solids were added after working pressure was reached, their time of contact with the solution was limited to the time of the run which was the same at all pressures. The temperature was constant during this time and was higher, the higher the pressure. Owing to differences in temperature conditions, comparisons cannot be made on the basis of time alone. The following reasoning, however, seems justified.

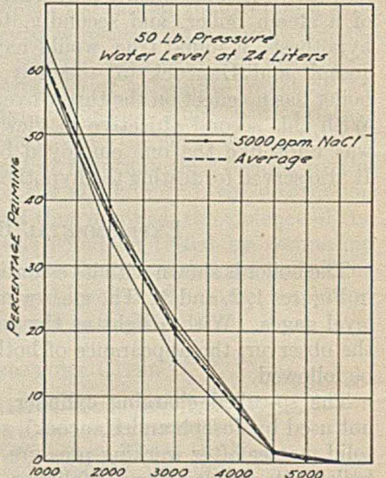


FIGURE 4. FOUR RUNS AND AVERAGE AT PRESSURE OF 3.5 KG. PER SQ. CM.

At 3.5 kg. per sq. cm. (50 pounds per square inch) the time of contact of solids with solution and the temperature of the solution were both relatively low; therefore little difference between the two procedures should be expected. At 5.3 kg. per sq. cm. the time of contact of the solids added in the cold was longer than at the lower pressure and a considerable difference in the priming is observed on comparing the hot and cold curves. As the pressure was increased, the time of contact with the solution was longer during the heating-up period of the cold addition, and the average temperature of the solution during this period was higher. This apparently compensated for the higher temperature during the run, so that no material difference is observed on the graphs at

Table I. Priming at Different Water Levels and Pressures

Water Level	Priming at 3.5 kg.			Priming at 5.3 kg.			Priming at 7.0 kg.			Priming at 10.6 kg.		
	S[a]	C	H	S	C	H	S	C	H	S	C	H
Liters	%	%	%	%	%	%	%	%	%	%	%	%
23	61	71	71	30	36	41	13	14	12	0	0	0
22	37	52	51	11	19	25	3	3	3	.	.	.
21	19	31	31	4	7	14	0.4	0.4	0	.	.	.
20	7	15	14	0.5	1	6	0	0	0	.	.	.
19.5	2	6	6	0	0	1	..	..	..	.	.	.
19.0	0.4	2	2	0	0	0	..	..	..	.	.	.
18.5	0.0	0.2	0.3	0	0	0	..	..	..	.	.	.
18.0	0	0	0	..	..	..	..	..	..	.	.	.

[a] S, salt alone; C, solids added to cold solution; H, solids added after working pressure was reached.

7.0 and 10.6 kg. per sq. cm., except during the first part of the runs.

The results at 7 kg. are out of step, in that they show less difference between the hot and cold additions than at 10.6 kg. No explanation of this can be offered at present, but it will be studied later. Since each curve is the average of four runs, it is not likely that experimental errors are the cause.

Different initial water levels were used in the experiments depicted in Figures 5 to 8, and therefore the results at the different pressures cannot be compared among themselves without calculating them to common levels. At first this plan of using different water levels appears to be bad experimentation; but more information was obtained thus, by starting in each case with as high a level as possible to give at the beginning of the run an ejectate high in percentage of boiler water, and still to show toward the end of the run some priming.

In Table I all results beginning with 24 liters in the boiler are tabulated.

Table I shows the marked effect of different pressures at the same water levels. Only the results at 7.0 and 10.6 kg. per sq. cm. are comparable among themselves, however, because in these experiments the initial water levels were the same. The results at 3.5 and 5.3 kg. cannot strictly be compared with those at the higher pressures because these were obtained after 3 liters of ejectate had left the boiler.

Miscellaneous Experiments

In experiments 1 to 4 below, 5000 p. p. m. sodium chloride solutions were used and 5000 p. p. m. powdered limestone, except as indicated. The pressure was 3.5 kg. per sq. cm. (50 pounds per square inch). Solids were added in the cold.

1. Effect of Returning All Ejectates to Boiler and Repeating the Run. This was done three times, making a total of four runs with the same solution and same solids. Each time a considerable reduction in priming was observed as compared with the preceding run, and in the third and fourth runs the priming was less than that of a salt solution containing no solids. This is discussed below.

2. Effect of Used Salt Solution and Fresh Solid Matter. The solution used in the last run in experiment 1 (both the residue in the boiler and the total ejectates) was filtered and returned to the boiler, and 5000 p. p. m. fresh solids were added. The priming was the same as when both salt solution and solids were used fresh.

3. Effect of Used Solids and Fresh Salt Solution. The boiler was washed and charged with fresh salt solution and the solids that had gone through the four runs of experiment 1. This solid matter had been filtered and washed with distilled water. The priming was less than that of a salt solution alone.

Experiments 2 and 3 show that the drop in priming was due to a change in the solid matter and not in the salt solution.

4. Effect of Small Amount of Fresh Solids Added to Spent Solids. The total ejectates from experiment 3 were returned to the boiler, and 2000 p. p. m. of fresh solids added. The mixture then consisted of 5000 p. p. m. spent solids, which not only did not increase priming but actually reduced it, and 2000 p. p. m. fresh solids, an amount which by itself would have had scarcely any effect. The priming was comparable with that of 5000 p. p. m. of fresh solids, particularly in the earlier part of the run.

This effect of fresh solids added to spent solids will be studied further because of its relation to boiler conditions under which fresh solids are constantly forming.

Solid Matter without Foam-Stabilizing Properties

Foulk and Hansley (2) showed that ground flint had no foam-stabilizing effect at atmospheric pressure because it is instantly wet and sinks. Comparison sets of runs (four each) were therefore made to test the effect at 7.0 kg. per sq. cm. (100 pounds per square inch) pressure. The results and essential data of the experiment are given in Figure 9.

The priming is distinctly less when the ground flint is present. This is due to the greater smoothness of boiling induced by the nonstabilizing solid. Furthermore, it makes no difference whether the solid employed is naturally a nonstabilizer or whether it has lost its stabilizing properties on long contact with the boiler water—for example, experiments 1 and 3 above. Close inspection of Figures 7 and 8 also shows that toward the end of the runs the priming is less with solids than without.

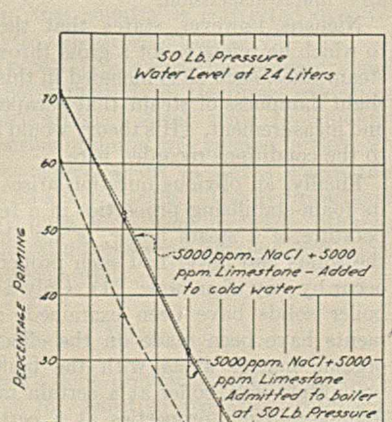


Figure 5. Effect of Powdered Limestone at Pressure of 3.5 kg. per sq. cm.

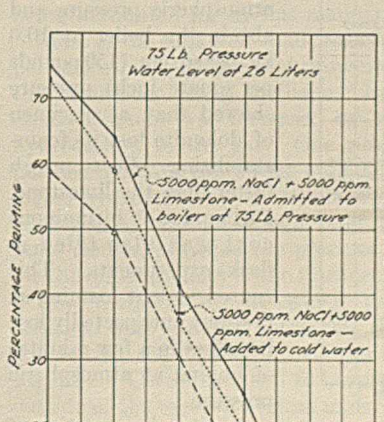


Figure 6. Effect of Powdered Limestone at Pressure of 5.3 kg. per sq. cm.

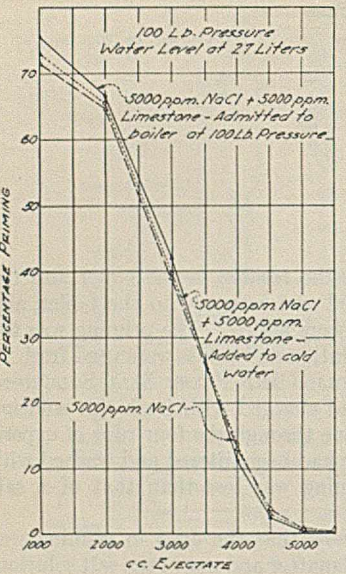


Figure 7. Effect of Powdered Limestone at Pressure of 7.0 kg. per sq. cm.

Discussion of Results

The point brought out here, that boiler solids, though initially possessing high foam-stabilizing properties, rapidly lose them at the high temperatures (pressures) of a steam boiler, is new. Only one other record of such an observation has been found. Holmes, in discussing a paper by Foulk (*1*), reported such a case in an experimental boiler and called it the "aging" of the sludge.

The cause of this loss of foam-stabilizing power as advanced in this and in a former paper (*2*) is a progressive lessening of the solid matter's resistance to wetting. If the solid wets instantly as in the case of ground flint, the particles sink at once and therefore do not collect on the bubble films and stabilize them. This resistance to wetting may be due to traces of oil in the solids, as in many boiler scales, and probably in the ground limestone used in these experiments. In some cases, however, it is a natural property of the material. For example, finely ground galena was found to have foam-stabilizing properties in boiling salt solutions and to be slower in losing these properties than any other material tried. This is interesting in showing that density of the solids plays a minor role.

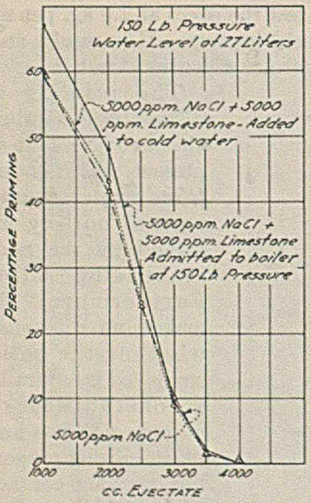


Figure 8. Effect of Powdered Limestone at Pressure of 10.6 kg. per sq. cm.

The rate of loss of resistance to wetting varies greatly. For example, experiments in a flask at atmospheric pressure and also in the boiler at 10.6 kg. per sq. cm. (150 pounds per square inch) pressure showed that a specimen of dolomite lost its foam-stabilizing effect much faster than the limestone. Pulverized bituminous coal was also tried in flask experiments. This caused violent foaming at first but unexpectedly lost its effect in a few minutes of boiling at atmospheric pressure.

A natural suggestion of course is to use boiler sludge in these experiments instead of material such as limestone. The matter is, however, not so simple as it seems at first. Any actual boiler sludge would probably have been in a boiler long enough to have lost its stabilizing properties, and therefore the use of old sludge is of doubtful value. A specimen of ground scale probably containing oil was nevertheless tried in a number of runs at 10.6 kg. It gave peculiar results. When first admitted to the boiler, it increased the priming, then decreased it, and toward the end of the run again increased it.

The results of Joseph and Hancock were confirmed when the conditions of the experiments were the same—namely, a not too brief time of contact between solids and salt solution. Their broad generalization that solids have no effect on priming cannot, however, be substantiated. Much more evidence must be brought into court before the final verdict on the guilt of solid matter in promoting priming can be rendered.

Both the dissolved salts and the suspended solids increased in concentration during a run. This was not measured, however, because in both cases the effect would be to increase the priming, and it was not believed that the comparability of the curves was materially affected.

A larger proportion of the finer than of the larger particles of the solids was carried over by the priming. This was also not measured because miscellaneous experiments 1 and 3 show that the loss of fine particles was not the determining cause of the loss of foam-stabilizing effect.

The theory of loss of resistance to wetting has been challenged by Niehaus (*4*) who gives results to show that the priming of a commercial water tube boiler was due to solid matter just on the border line between colloidal dispersion and macrosuspension.

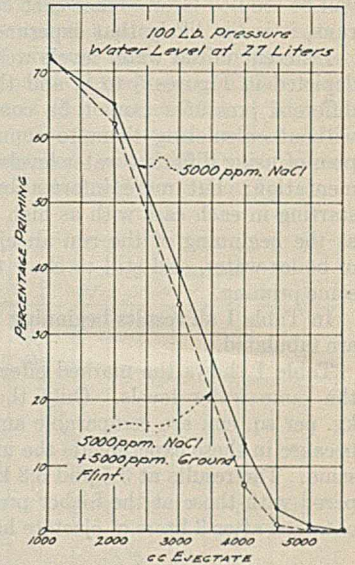


Figure 9. Effect of Ground Flint at Pressure of 7.0 kg. per sq. cm.

Niehaus, however, states that the foaming and priming to which he refers is not a gross throwover of water into the steam lines, such as is included in this paper, but rather that slight dampness of steam that escapes ordinary observation and measurement. His theory would therefore scarcely apply to the conditions recorded here.

Finally, an obvious question arises: If solid matter loses its foam-stabilizing properties in a few minutes at the temperature of a steam boiler, is not the effect the same as if the solids had never had such properties? Two suggestions occur by way of answer: (1) Only a small number of actual boiler solids have been examined, and almost no experiments have been made on the effect of small amounts of organic matter along with the boiler solids. (2) Solids precipitate in a boiler at a certain rate, and they lose their foam-stabilizing properties at a certain rate. These rates vary independently, and it is easy to imagine that some ratios of the two rates will increase priming and other ratios will not. The authors at least hope that the new facts brought to light in this investigation may help in understanding some of the obscure problems in the behavior of boiler water.

Acknowledgment

Grateful acknowledgment is made to the Joint Research Committee on Boiler Feedwater Studies under whose auspices this investigation was made; to the Ohio State University Engineering Experiment Station for valuable assistance; and especially to the Engineering Research Foundation which furnished the funds for the equipment used and for a research assistant.

Literature Cited

(1) Foulk, *Trans. Am. Soc. Mech. Eng.*, RP-54-5 (1932).
(2) Foulk and Hansley, Ind. Eng. Chem., 24, 227 (1932).
(3) Joseph and Hancock, *J. Soc. Chem. Ind.*, 46, 315T (1927).
(4) Niehaus, Doctor's Dissertation, Buchdruckerei Theodor Lambertz, Krefeld, Germany, 1932.

Received September 26, 1933.

Direct Oxidation of Saturated Hydrocarbons at High Pressures

Peter J. Wiezevich and Per K. Frolich, Standard Oil Development Company, Elizabeth, N. J.

Natural gasoline hydrocarbons have been oxidized at high pressures to produce a number of useful derivatives. Laboratory and semi-commercial plant data are submitted on the use of methane, ethane, propane, butanes, pentanes, and heptanes as raw materials for this purpose. The products obtained may be separated into fractions having narrow boiling ranges.

Oxidation of methane at relatively high temperature results in the production of some methanol. Higher hydrocarbons undergo a carbon-carbon scission during oxidation with the formation of lower derivatives in high yields. Recirculation of intermediate derivatives may be resorted to for the manufacture of acids as main products.

Increase in pressure tends to lower the temperature at which oxidation takes place. Furthermore, the decomposition of intermediate products is greatly retarded by this means.

THE possibility of obtaining commercially valuable products by direct oxidation of saturated hydrocarbons has been the subject of considerable discussion and debate. Although it has been successfully applied to the aromatics such as benzene, naphthalene, and anthracene, no real progress has been made with the aliphatic hydrocarbons, in spite of the enormous amount of work done in this field (*14, 23, 24, 48, 66*). Mention has been made in the literature of a few commercial installations for the manufacture of oxidation products of natural gas (*19*) and kerosene (*9*). In spite of the fact that formaldehyde is considered the main primary oxidation product of methane, about 40 per cent of the synthetic methanol at present produced from hydrogen and oxides of carbon in this country is converted over to formaldehyde by catalytic dehydrogenation (*27*).

In line with a general research program, this company some time ago undertook a thorough study of the direct oxidation of light saturated hydrocarbons. After some preliminary laboratory work, an experimental unit was erected in 1926–27 in the vicinity of a casinghead plant in Texas where the processes were tried out on a larger scale. The hydrocarbons oxidized in a relatively pure state were methane, ethane, propane, butane, pentane, and heptane; a detailed discussion of each will be taken up separately.

Previous Work

A good deal of the work done previously appears to have centered in the search for selective oxidation catalysts. Among those which have been studied are copper and silver (*66, 68, 69*), iron (*62*), tin compounds (*53*), alkali metal compounds (*41*), metallic oxides (*42, 43, 45, 54*), phosphates and borates (*34, 55*), other metals (*44, 85*), and salts (*12*), as well as chlorine (*18, 19, 51, 53, 55*), silica gel (*66*), asbestos, pumice (*90*), etc.

The oxidizing media used have been air, oxygen (*24, 40, 45, 71*), ozone (*23, 25*), nitrogen oxides (*6, 27, 49, 69*), carbon dioxide (*25, 39, 50, 51, 90*), and other reagents (*24*). In order to control the speed of the reaction, diluents such as nitrogen (*21, 51, 90*), hydrocarbons (*24*), steam (*43, 67, 69, 92*), and hydrogen (*37*), have been tried. Studies on the oxidation of hydrocarbons also have been made under silent electric discharge (*23*), radiation (*50*), and ultraviolet light (*56*).

Oxidation of Methane and Ethane

Laboratory experiments only were made on methane and ethane. The assembly of the apparatus used was similar to that shown in Figure 1, which is self-explanatory (*75, 86*). Some of the data obtained for these hydrocarbons are shown in Table I. Since it was difficult to measure the exact amounts of hydrocarbon used in these experiments, material balances were made on the exit products, usually only about 70 per cent of the inlet oxygen being accounted for in this manner.

Most of the runs were made on a natural gas containing 2.1 per cent ethane, 6.3 per cent propane, and 5 per cent nitrogen, the remainder being methane. In some experiments the ethane content was increased by the addition of the pure hydrocarbon to the gas. One run was made on specially purified methane containing only 0.36 per cent ethane and no higher hydrocarbons. The oxidizing medium was 99 per cent oxygen in all cases, although, later, air was found to give the same results, provided the pressure was increased to correct for the diluting effect of the nitrogen.

The temperatures at which measurable reaction was obtained were found by increasing the temperature gradually and noting the change in exit gas analysis, as indicated in Figure 2. Care was taken to keep the oxygen concentration outside of the explosive limits under the operating conditions (*20*); otherwise, explosions were apt to occur.

The liquid product was condensed under pressure and analyzed by chemical means as well as by fractionation. The exit gas, generally containing about 1.5 per cent carbon dioxide, 1.0 per cent hydrogen, and some unconsumed oxygen, was also scrubbed with water to recover as much of the oxidation products as possible.

Effect of Catalysts. Generally, metallic catalysts such as calcium, chromel, silver, and aluminum gave better results than empty tubes.

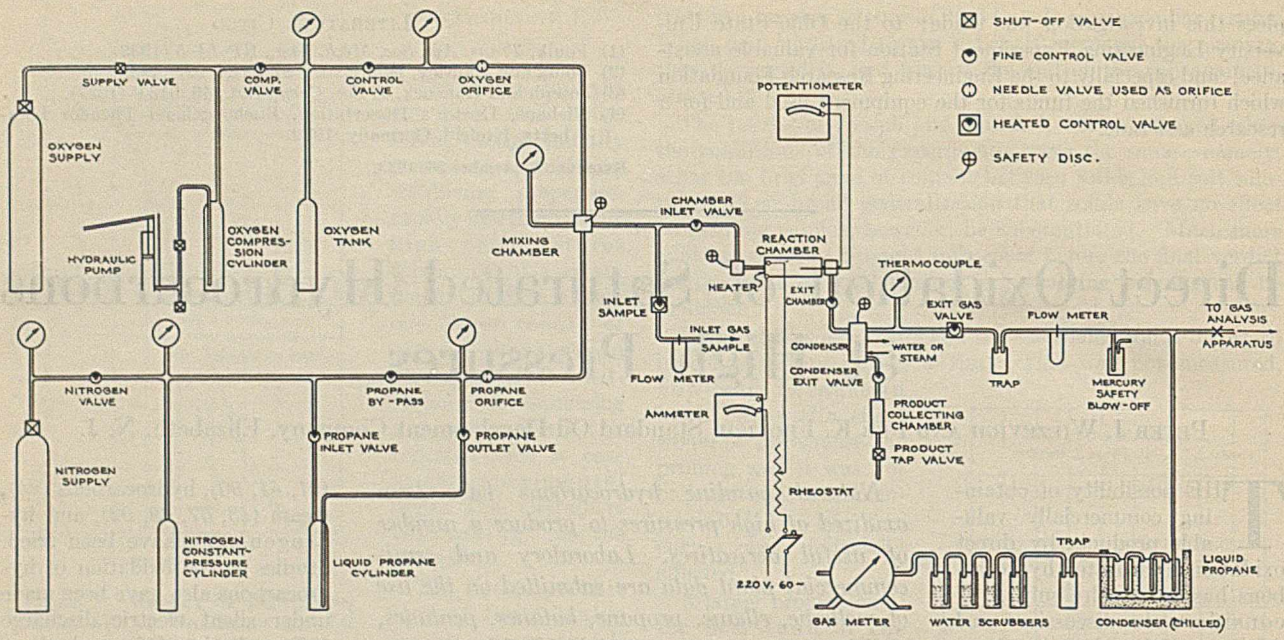


FIGURE 1. APPARATUS FOR HIGH-PRESSURE OXIDATION OF HYDROCARBONS

EFFECT OF PRESSURE. Blank runs made at 400° to 700° C. at atmospheric pressure showed only traces of methanol and formaldehyde. As would be expected, the effect of increased pressure is to increase the amount of methyl alcohol in the product. However, although the yield of methyl alcohol still continued to rise, the rate of increase of the total oxygen efficiency and carbon conversion to desirable products (methyl alcohol, formaldehyde, and formic acid) fell off with increasing pressure. Most of the experiments were made at 135 atmospheres.

EFFECT OF RATE OF FLOW. In the range investigated, increase in rate of flow through the reactor resulted in a corresponding increase in output of desirable products, but the total oxygen efficiency or carbon conversion were not altered to any appreciable extent. The limit at which the rate can be increased is determined by the ability to supply the necessary heat to the gases, since, even though the reaction is exothermic, it is not sufficiently so to support itself with the concentrations of oxygen used in the present equipment, usually in the range of 5 to 8 per cent.

EFFECT OF TEMPERATURE. Increase in temperature from 300° to 500° C. tended to produce more carbon monoxide, carbon dioxide, and formic acid at the expense of the other products. The minimum temperature at which reaction took place at a reasonable rate was about 370° C. at 135 atmospheres pressure in the case of ethane oxidation, while for methane it was in the neighborhood of 500° C. Recently, lower reaction temperatures have been reported by Newitt and Townend (*58A*).

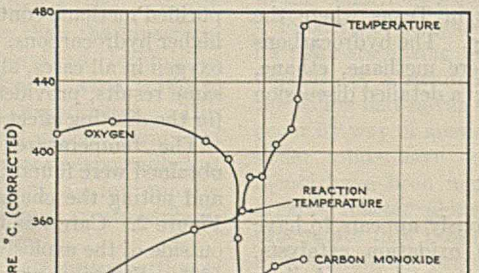


FIGURE 2. TIME CURVES FOR DETERMINATION OF REACTION TEMPERATURE FOR NATURAL GAS

EFFECT OF GAS COMPOSITION. As mentioned previously, most of the experiments were performed with a natural gas at 300° to 500° C. Of the desirable products formed, methyl alcohol was present in preponderance, generally in quantities of three to eight times the amount of formaldehyde. Some formic acid was also formed, as well as considerable amounts of water. At the time the experiments were performed, it was believed that the products were obtained by the oxidation of the methane, but a later run on purified methane showed that the temperatures employed (300° to 400° C.) were too low for methane to react, and therefore the products were mainly due to the ethane present. This observation was substantiated later when increasing amounts of ethane were added to the reacting gas. Thus, Figure 3 shows how the amount of methyl alcohol in the product increased with the ethane concentration, and that the main product of the oxidation of ethane was methyl alcohol. Some ethyl alcohol was also produced, generally in the ratio of one part of ethyl to ten or twenty of methyl alcohol.

As mentioned previously, one run was made on natural gas carefully purified by rectification at low temperature so that the ethane content was reduced to 0.36 per cent. Except for about 7 per cent nitrogen, the ethane was the only impurity. In this case it was found that the lowest temperature at which reaction could be observed was about 520° C. even at 135 atmospheres pressure. Since the temperature was high, a good deal of the desirable products decomposed so that most of the liquid recovered consisted of water. However, it was shown that twice as much methyl alcohol was formed during the experiment as could be accounted for if all of the ethane present as impurity reacted quantitatively to produce only methyl alcohol. Since such quantitative conversion has never been approached, this actually means that the alcohol must have been formed by the oxidation of methane.

YIELDS. With a natural gas containing 2.1 per cent ethane and 0.3 per cent propane, a characteristic run at 135 atmospheres pressure, with 5.4 per cent inlet oxygen concentration and a temperature of about 390° C., produced a liquid product of specific gravity 0.953, analyzing about 30.3 per cent methyl alcohol, 3.3 per cent formaldehyde, and 0.5 per cent formic acid. In this case 16.2 per cent of the inlet oxygen was present in the desirable products and 3.7 per cent of the ingoing carbon (including the methane) was converted to methyl alcohol, formaldehyde, and formic acid. When including the products recovered in the scrubber water, one cubic meter of such natural gas would yield 0.0615 liter of methyl alcohol, 0.008 liter of formaldehyde (calculated as liquid), and 0.0004 liter of formic acid.

Oxidation of Propane

Since propane is a liquid at the pressures employed, advantage was taken of the relatively high solubility of air in the hydrocarbon to effect a constant oxygen concentration as well as to avoid any explosion hazard in the reactor (*82*). As shown in Figure 4, the air dissolves in the propane to produce a mixture containing about 7 mole per cent oxygen at 140 atmospheres pressure. The solubility increases somewhat in the case of pentane and butane. Oxygen is much more soluble in the hydrocarbons than nitrogen, and the solubility is not altered greatly when the temperature is raised to 90° C. It was also found that the presence of dissolved nitrogen did not affect the solubility of oxygen in the hydrocarbon to any appreciable extent. Use was made of this property to enrich the oxygen content of the liquid propane by bleeding off nitrogen from the top of the saturator.

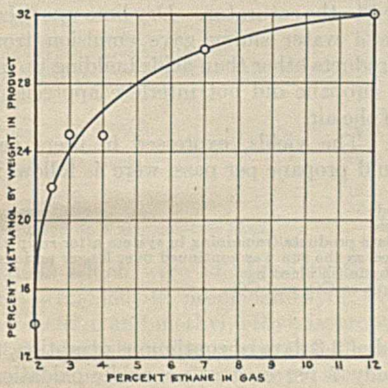


Figure 3. Effect of Ethane Added in Natural Gas upon the Percentage of Methyl Alcohol in the Oxidation Products

Catalyst, nickel; inlet oxygen, 6 per cent; pressure, 2000 pounds per square inch (140.6 kg. per sq. cm.).

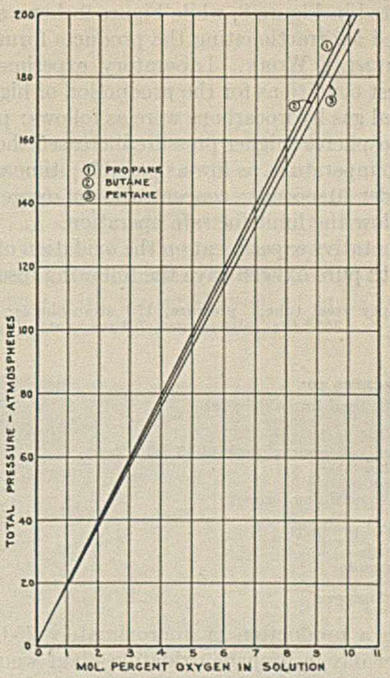


Figure 4. Effect of Pressure on the Solubility of Air in Hydrocarbons at 20° C.

The semi-commercial plant is shown in Figure 5, the casinghead plant furnishing the raw materials being located in the background. In the foreground can be seen the pits in which were placed the preheater and reactor. All high-pressure equipment, with the exception of the compressor (which was located in the large building), was placed in pits having walls of concrete extending about 6 feet (1.8 meters) above the level of the ground. The saturator pit containing the vessel wherein the hydrocarbon was saturated with air is seen in Figure 6, which shows also the remote control and automatic devices, as well as the indirect means for noting the liquid level. The propane, butane, etc., were fractionated out of the casinghead in a 24-inch (61-cm.) packed column and then redistilled.

One type of reactor, shown in Figure 7, was constructed to facilitate by-passing various loops of 2.5-cm. high-pressure tubing. After passing through this reactor, the gases were run into the intermediate coolers (shown on top). The scrubbers for removing the products from the hydrocarbon

Table I. Oxidation of Methane and Ethane

Run	CH_4 + Following % C_2H_6:	Pressure	Exit Gas Rate	Inlet Oxygen	Temp.	Catalyst	Liquid Product	O_2 to Useful Products
		Atm.	Liters/hour	%	° C.		% by weight	%
44	2	135	68	8.1	410	Iron	35 CH_3OH	CH_3OH, 11.7; others, 3.5
136	0.36	133	132	6.8	520	Nickel	16.4 CH_3OH	..
52	2	132	70	8.6	410	Aluminum	28.7 CH_3OH 7.4 CH_2O 1.3 CH_2O_2	18
74A	2	130	135.5	3.0	300	None	29.2 CH_3OH 7.9 CH_2O 1.7 CH_2O_2	14.1
97	2.5	132	52.3	5.7	355	Nickel	21.9 CH_3OH 3.9 CH_2O	11.1
100	7	131	51.0	6.1	385	Nickel	30.0 CH_3OH	..
102	12	132	48.5	5.2	389	Nickel	28.2 CH_3OH 6.8 CH_2O 0.3 CH_2O_2	15.0
104	22	130	34.5	5.0	390	Nickel	30.0 CH_3OH 6.0 C_2H_5OH	14.4
105–6	22	131	58	6.0	392	Iron	32 CH_3OH 4 C_2H_5OH 1.5 higher alcohols 6 below 66° C.	..

are illustrated in Figure 8, while Figure 9 shows a sixty-plate column used for fractionating the products formed (*83*, *85*).

Experimental Work. Laboratory experiments showed that the best conditions for the production of higher alcohols from natural gas hydrocarbons were as follows: pressure, 130 to 200 atmospheres (higher pressure increased the yields only slightly); temperature, as low as possible; time of heating in reactor, under 10 seconds; concentration of oxygen, as high as possible below the limit for safe operation.

A representative experiment on the oxidation of 98 per cent propane with pure oxygen gave the following results:

(Reactor, empty steel tube; pressure, 170 atmospheres; temperature, 350° C.; inlet oxygen, 7.9 per cent)

Oxygen Converted to:		O_2 Converted %
Acetaldehyde (and formaldehyde)		9.4
Acetone		2.3
Methyl alcohol Ethyl aclohol Propyl alcohol	approx. ratio of 13.4:8:5.2	26.6
Butyl alcohol		0.7
Acetic acid (containing formic)		4.1
Total useful products		43.1
Carbon dioxide		10.1
Carbon monoxide		9.7
Water		30.7
Unconverted oxygen		7.0

Assuming a production of approximately 25,000 liters of products per day, a propane oxidation plant would yield the following amounts of the various compounds:

	Liters/day		*Liters/day*
Formaldehyde	210	Alcohols	16,000
Acetaldehyde	4,200	Acetic acid (containing formic)	1,360
Acetone	1,960		

The variation of reaction temperature of propane and oxygen with pressure was studied in an Enduro 18-8 reactor immersed in a lead bath. A long time of contact was employed, the oxygen concentration being 6 per cent. The following results show that increase in pressure lowers the temperature at which appreciable reaction is noticed:

Pressure *Atm.*	Reaction Temp. (Lead Bath Temp.) ° *F.* (° *C.*)
150	235 (112.8)
67	290 (143.3)
33	305 (151.7)

Acid Production. Instead of removing all of the products formed, several runs were made in which only the acids were removed by neutralization, while the other products were recirculated with the hydrocarbon until they were also converted to acids (*79*). The following scheme (Figure 10) was tried out on a larger scale: The liquid propane, which in this case contained some 3 to 7 per cent ethane and 3 to 7 per cent higher hydrocarbons, was saturated with air at a pressure of 133 atmospheres by forcing the hydrocarbon by means of a high-pressure steam pump at a rate of 7.6 liters per minute into a bubble plate column, the average oxygen concentration of the liquid propane leaving the column being about 5 to 6 mole per cent. The propane thus saturated with air was sent through the preheater which was immersed in a naphthalene bath kept at about 175° C. and allowed to enter the reactor immersed in a lead bath at 400° C.

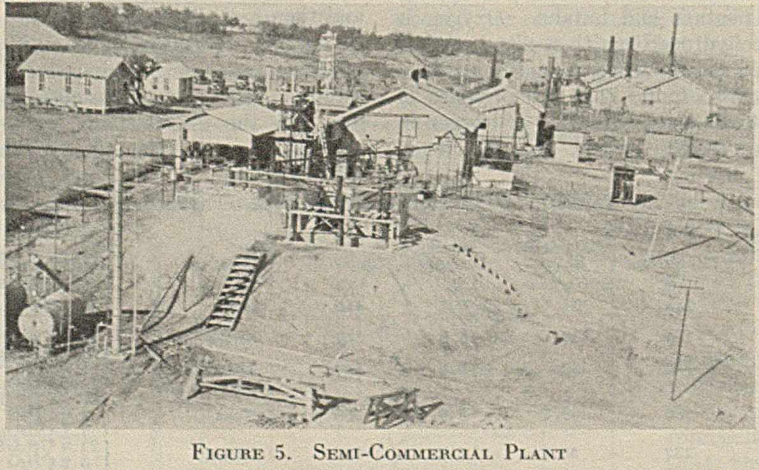


Figure 5. Semi-Commercial Plant

From the reactor, the stream passed through a condenser and then to a steam-heated reducing valve where the pressure was decreased from 133 to 20 atmospheres. The propane plus product then passed into the aqueous layer separator where the water layer (containing about 40 per cent of the total acid) was removed and the reacted propane (containing liquid products in solution) was allowed to enter the gas bleed tank to strip out the permanent gases. This was accomplished by running the mixture around coils cooled by the expansion of an ethane-propane mixture.

The water layer was withdrawn from the separator intermittently to a storage tank and subsequently charged to a chrome-nickel steel fractionating column, where the products other than acids and water were distilled off and returned to the reactor for further oxidation. The bottoms from the still were analyzed for acetic and formic acids and neutralized with lime.

After leaving the gas bleed tank the reacted propane was neutralized with dry lime in a semi-continuous neutralizer and returned to the saturator. Dry lime was used because in many cases a water slurry gave emulsion troubles. The oxidation products other than acids building up in concentration in the propane did not interfere appreciably with the solubility of the air.

Results. The yields, expressed in liters per thousand liters of liquid propane per pass, were as follows:

Acetic acid	1.5
Formic acid	1.1
Intermediate products (remaining in system after run; these decreased as the run was continued over longer periods)	8.0
Formaldehyde (in bleed gas)	0.4
Propane lost as CO_2 and CO	7.0
Water	9.5

At the end of 3.3 days of continuous operation, the propane contained only 7 per cent of nonacidic oxidation products. About 80 per cent of the total intermediate products remained undissolved in the propane. An examination of these showed that they were mainly methyl alcohol, ethyl alcohol, and acetone. Of the total acids made, 46 per cent by volume was formic. This corresponds closely to an equimolecular yield of formic and acetic acids. Acids higher than acetic kept building up from 9 per cent by volume of total acids to about 14 per cent toward the end of the runs.

It can be seen that even at the high pressure employed, the oxidation reaction causes the formation of appreciable quantities of products other than alcohols, such as aldehydes, acids, and water. Furthermore, the greater the number of carbon atoms in the hydrocarbon molecule, the greater also is the possibility of more products to occur. Thus, in the oxidation of propane, a mixture containing propyl alcohol, ethyl alcohol, acetone, acetaldehyde, formic acid, methyl alcohol, and water resulted in which the ethyl alcohol-propyl alcohol fraction was present in greatest quantity. It is also apparent that higher oxygen efficiencies are possible with higher hydrocarbons than with lower ones.

It was found that by recirculation of the alcohols, etc., with the propane through the reactor, only acids were recovered. These acids were removed as salts without much contamination by neutralization of the propane with dry lime.

OXIDATION OF BUTANE

EXPERIMENTAL WORK. The apparatus employed was essentially the same as in the case of propane oxidation. The reaction temperature of the 98 per cent *N*-butane was found to vary with pressure in the same manner:

PRESSURE	TEMP. (LEAD BATH TEMP.)
Atm.	° *C.*
160	210
100	220
67	235
33	255

Characteristic data of the laboratory experiments on 95 per cent butane are as follows:

Run No.	232	263
Oxidizing gas	Air	Oxygen
Inlet oxygen concn.,[a] mole %	6.2	6.4
Pressure, atm.	160	140
Temperature, ° C.	410	281
Rate of exit gas, liters/hour (at N. T. P.)	155	126
% entering oxygen converted to:		
Alcohols (methyl, ethyl, propyls; ratio about 1:2:3)	21.9	18.6
Butyl alcohol	1.5	1.0
Acetic acid	8.7	11.2
Aldehydes	6.1	16.4
Total useful products	38.2	47.2
Water	18.5	21.0
Gaseous products	37.8	29.5

[a] Analysis reported on a nitrogen-free basis.

The products which were identified in the oxidation of butane were: acetaldehyde, propionaldehyde, acetone, acetic acid, propyl acetate, and methyl, ethyl, isopropyl, *N*-propyl, and isobutyl alcohols. The methyl-ethyl-propyl alcohol fraction was in preponderance with propyl alcohol as the main constituent.

The effect of pressure upon the types of products produced when oxidizing pure *N*-butane is illustrated as follows:

INLET OXYGEN GOING TO:	PER CENT OF OXYGEN At 33 atm.	PER CENT OF OXYGEN At 133 atm
Acetone	1.4	0.7
Methyl alcohol	15.0	8.4
Ethyl alcohol	2.5	6.3
Propyl alcohols	3.2	8.9
Butyl alcohols	0.6	2.5
Aldehydes	6.9	15.9
Acids	16.7	4.6
Total useful products	46.3	47.3
CO_2	9.4	6.1
CO	3.8	9.4
Unconverted oxygen	15.0	9.0

Low pressure tends to cause the formation of lower alcohols and acids; high pressure favors the formation of higher alcohols and aldehydes.

ACID PRODUCTION. As in the case of propane, the butane and intermediate products were recirculated and only the acids were removed from the system by neutralization with dry lime. The runs were made at 130 to 185 atmospheres pressure, 5 to 7 mole per cent inlet oxygen concentration, 315° to 395° C. reactor temperature, and a butane circulation rate of about 7.6 liters per minute.

The yields of products, based as liters per 1000 liters of liquid butane circulated per pass, were as follows:

Formic acid	0.62
Acetic acid	3.62
Formaldehyde	0.20
Intermediate products (removed after run)	4.9
Water	6.3
CO_2, cu. m. at N. T. P.	4.23
CO, cu. m. at N. T. P.	4.32

The amount of formic acid present in the total acids appeared to increase with increase in isobutane content:

ISOBUTANE	FORMIC ACID
%	% *by vol.*
0	10.2
5	13.1
15	18.2

OXIDATION OF PENTANES

EXPERIMENTAL WORK. A flow sheet employed in the large-scale high-pressure oxidation of substantially pure pentane (about sixty parts normal to forty parts isopentane) is shown in Figure 11. Two schemes were employed. The first consisted in the formation of alcohols as major products; the other dealt with the production of acids only. These processes will be taken up separately.

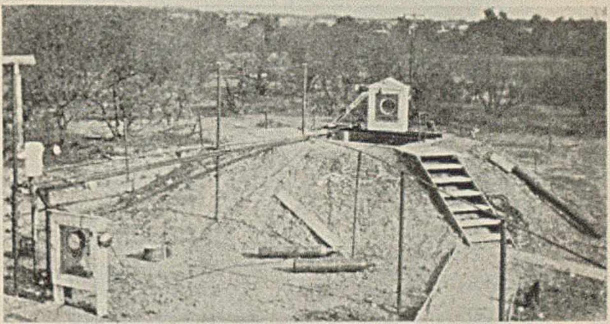


FIGURE 6. SATURATOR PIT

EXPLOSIVE LIMITS. The explosive limits for pentane-air and pentane-oxygen mixtures obtained according to the method described by Cooper and Wiezevich (*20*) were as follows:

MIXTURE	TEMP.	TOTAL PRESSURE	LIMIT MIXTURE
	° *C.*	*Atm.*	*Mole %*
Pentane-oxygen	23	53.3	14.5
Pentane-oxygen	90	50.0	12.1
Pentane-air	20	333.3	18.2

ALCOHOL PRODUCTION. Although the main products of this method were alcohols, it must be borne in mind that other products such as aldehydes, acids, and acetone were produced in appreciable quantities. As shown in Figure 11, saturation of the pentane was effected at a pressure of 200 atmospheres in an eleven-plate bubble-cap saturator having one 10-cm. cap per plate. Under these conditions the saturated pentane contained from 5 to 6 mole per cent of oxygen. Tests made on this vessel indicated that saturation was obtained on the first few plates.

The saturated pentane, preheated to about 180° C. in a steel coil immersed in boiling naphthalene, was introduced into a steel reactor which was kept at about 240° C. by a boiling diphenyl oxide bath. At this point it was mixed with a small air-free pentane stream which was superheated to about 550° C. by a lead bath, serving to start the reaction and to give a better control of the temperature. The pentane and products were condensed in a chrome-nickel steel condenser and run into a neutralizer.

Under these conditions the time of heating in the reactor was calculated to be about 80 seconds. It was felt, however, that a decrease of time of heating to a fraction of a second might lower the decomposition of the products to an appreciable extent and, consequently, in one experiment the 7.61-cm. reactor was plugged with a 7.30-cm. steel shaft, giving an annular space of about 0.16 cm. With this system the time of heating was reduced to 0.05 second. However, no reaction could be realized even with the highest possible temperatures.

Neutralization with lime was introduced in the pentane plus product stream between the aqueous layer separator and the

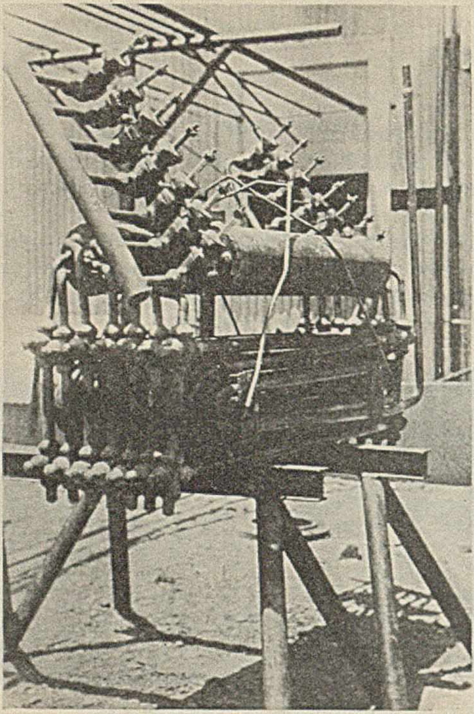


Figure 7. Reactor

scrubbing towers. The first neutralizer consisted of a 3000-liter horizontal tank half filled with thick lime slurry containing enough lime to take care of all the acid formed during the run. The pentane plus product stream was introduced through a perforated pipe at the bottom of the tank, and considerable agitation was obtained, mainly because of the nitrogen present in the mixture leaving the reactor. The main difficulty with this system was that very stable emulsions were formed. It was found, however, that emulsification could be avoided and good neutralization effected by countercurrent circulation of a dilute lime slurry through a packed column filled with pentane which was always kept on the acid side (about 0.1 per cent acid).

The neutralized pentane was then scrubbed to remove the oxidation products. A 90 per cent aqueous solution of methyl alcohol corresponding to 15–25 per cent of the pentane was found very efficient for taking out most of the compounds present. The pentane was then washed with water to remove dissolved methyl alcohol. However, water scrubbing was later substituted for methyl alcohol scrubbing, owing to the fact that considerable losses of the latter occurred and also that methyl alcohol scrubbing caused the formation of complex constant-boiling mixtures of pentane and the lower boiling products in the distillation step. Although water in amounts equivalent to 50 per cent of the pentane was not as efficient a scrubbing medium, the other products were recovered by continuous distillation of 15 per cent of the recycle pentane stream. Fractionation tests on the mixture of products in a sixty-plate column demonstrated that rerun stills would be necessary if very pure products were required.

The final method resorted to in preparing pure products from the aqueous extract was as follows: The products were first distilled out of the water, and the distillate, containing about 50 per cent water, was fractionated in a sixty-plate column. A crude acetaldehyde cut was obtained which, upon rerunning, produced a very pure grade of acetaldehyde. The bottoms from the rerun still were combined with the main bottoms, and a crude methyl alcohol–acetone cut was fractionated off. (This is a constant-boiling mixture of methyl alcohol and acetone containing about 15 per cent of the former.) This cut was also rerun, leaving some methyl alcohol in the bottoms in an attempt to keep the product free from ethyl alcohol. The product from the rerun consisted of fairly pure methyl acetone boiling between 54° and 64° C. The bottoms were again combined with the main bottoms, and a cut was made when a double layer was obtained in the distillate. This fraction, called the "intermediate cut," consisted mainly of ethyl alcohol and propyl alcohols, although some methyl and some higher alcohols were present and were later removed by rerunning. This cut boiled between 70° and 94° C. (dry). The next fraction, consisting of alcohols and esters of limited miscibility with water, was further fractionated until no layer separation occurred in the condensate, indicating that the products were substantially anhydrous.

The last product (higher alcohols) possessed a brownish red color and aldehydic odor. These objectionable properties were removed by treating with 25 per cent by volume of 25 per cent caustic soda solution and refluxing in a still for about 3 hours. After cooling, the caustic layer was removed from the higher alcohols, and the latter were then steam-distilled and dried by the double-layer drying method. This material, when so dried, boiled between 70° and 120° C.

Yields. A conservative figure for the daily yields of various anhydrous products, based upon runs of 7.6 liters per minute pentane flow, are as follows:

	Liters
Acetaldehyde (b. p., 19.5–20.5° C.)	23.7
Methyl acetone (b. p., 53–64° C.)	54.1
Intermediate alcohols (up to 80° C.)	71.0
Intermediate alcohols (80–110° C.)	46.4
Higher alcohols (110–130° C.)	37.5
Acetic acid	98.5

The intermediate product consisted mainly of a mixture of ethyl, propyl, and small amounts of *tert*-amyl alcohols. while the finished higher alcohols were composed mainly of *sec*-amyl and small amounts of *tert*-amyl alcohol. The acids obtained were composed of acetic and formic acids in a volume ratio of about 92:8. The pentane balances showed an average consumption of 1.7 liters of pentane per liter of product produced.

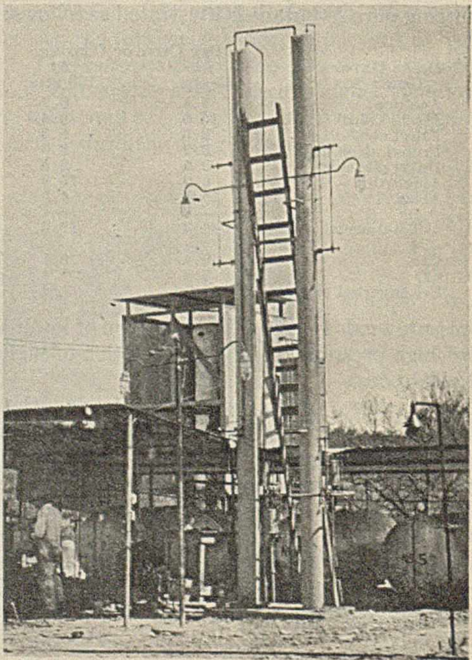


Figure 8. Hydrocarbon Scrubbers

Acid Production. As with propane and butane, runs were made in which the products were recirculated and oxidized, only acids being removed by neutralization with lime. As the products built up in the pentane, the solubility of the air was gradually decreased to about 4 to 5 mole per cent oxygen in the inlet mixture at 135 atmospheres. At the end of the runs an oxidized product remained which resisted the oxidation throughout the period of recirculation. This product was examined and found to consist mainly of tertiary alcohols and 4–5 carbon atom ketones, showing that these compounds were the most stable under the conditions of operation.

As stated previously, without recirculation the acid composition was approximately 92 per cent acetic and 8 per cent formic. With recycling, however, the composition of the acids was altered as follows:

Acid	*% by vol.*	Acid	*% by vol.*
Formic	20	Propionic	14
Acetic	53	Higher	13

About 7 liters of acids were produced per 1000 liters of pentane per pass. The losses as carbon dioxide and carbon monoxide in the gas amounted to about 2 liters of pentane per 1000 liters per pass.

The acids were best recovered from the calcium salts by regeneration with dry hydrogen chloride (85 per cent yield) and then purified by vacuum distillation. Analysis for formic acid was made by the A. O. A. C. method (*3*), and the other acids were determined by the Duclaux values (*22*, *30*, *39*) and boiling points of the butyl esters. Practically no unsaturated acids were found present.

Oxidation of Heptanes

The products obtained by pentane oxidation consisted mainly of 2 and 3 carbon atom compounds. For this reason it was believed that, if a hydrocarbon such as heptane were oxidized, the main portion of the products would be in the amyl alcohol, or 5 carbon atom range. The heptane used was actually a close-cut fraction boiling from 70° to 97° C. and included nearly all of the heptane isomers present in the casinghead gasoline.

Attempts were made to react the heptane in the reactor used for pentane, but even at a rate of 2.84 liters per minute, no success was obtained. It appeared that the time of heating was insufficient for reaction. The reactor finally employed was a steel coil formerly used as a preheater. In this coil both preheat and reaction were obtained, the temperature of reaction depending upon the rate of flow. At 2.84 liters per minute and 135 atmospheres pressure, reaction could be obtained at temperatures as low as 180° C. At a rate of 4.73 liters per minute, the average reaction bath temperature maintained was 225° C. Even this temperature was lower than the critical temperature of *N*-heptane which is 267° C., indicating that reaction was obtained in the liquid phase.

Neutralization was affected in the same manner as described under pentane oxidation. Since no extracting medium was available which would remove oxidation products from the hydrocarbon, recourse had to be taken to some other means of separation. It was found that methyl alcohol and heptane formed a constant-boiling mixture at about 57° C., which separated out in two phases. The composition of this mixture was about 60 per cent by volume methyl alcohol and 40 per cent heptane. Since only small amounts of products boiling below 70° C. were formed when heptane was oxidized, it was felt that this methyl alcohol distillation offered the best means of separation.

After neutralization, the heptane plus product was fed into a 75-cm. diameter Everdur bubble-cap still. Methyl alcohol was added, and the distillate was allowed to separate into two layers. The bottom methyl alcohol layer was returned to the still, while the top heptane layer, containing about 3 per cent dissolved methyl alcohol, was run into a packed column and fractionated until no methyl alcohol was present in the bottoms. The distillate was then returned to the first still while the hydrocarbon bottoms were recirculated to the oxidation system.

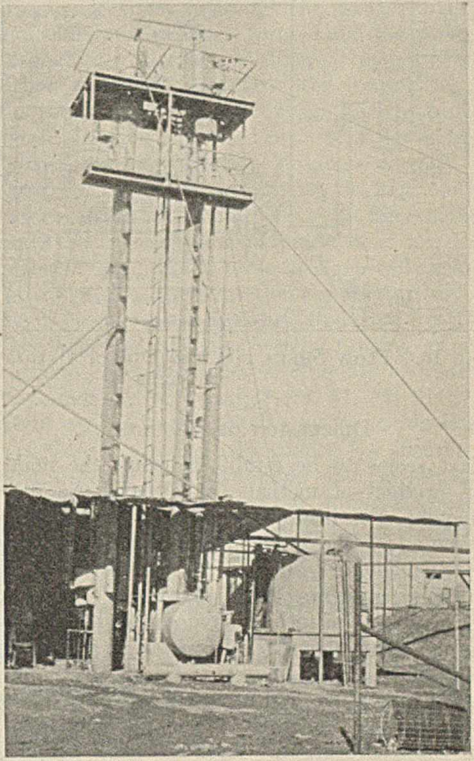


Figure 9. Sixty-Plate Fractionating Column

At the end of the run, the bottoms from the first still containing the products were distilled with methyl alcohol until hydrocarbon-free, the later methyl alcohol fractions being freed from hydrocarbon by dilution with water. This system gave very little trouble and the loss of methyl alcohol at the end of the run was quite low.

Results. Instead of obtaining amyl alcohols in predominating amounts, the product consisted mainly of alcohols in the hexyl-heptyl range boiling between 140° and 180° C. These results differing from pentane to such a degree may be due to the fact that reaction occurred in the liquid phase.

Expanding to an 1100 liter per minute circulation rate, the amounts of products obtained per day by the oxidation of heptane under these conditions would be:

	Liters		*Liters*
Aldehydes	170	Higher alcohols (up to 140° C.)	1100
Methyl acetone	1155	Higher alcohols (above 140° C.)	4860
Intermediate alcohols	2310	Calcium salts	4480 kg.

Corrosion Troubles

Considerable corrosion was experienced with the various oxidation processes tried on a large scale. Ordinary steel could not be made to last one month of continuous service; especially was this true in the high-pressure condensers. Of the materials tried, high-chromium nickel steels, such as Allegheny metal, gave the best service. Everdur, monel metal, and copper also gave good resistance to this type of corrosion.

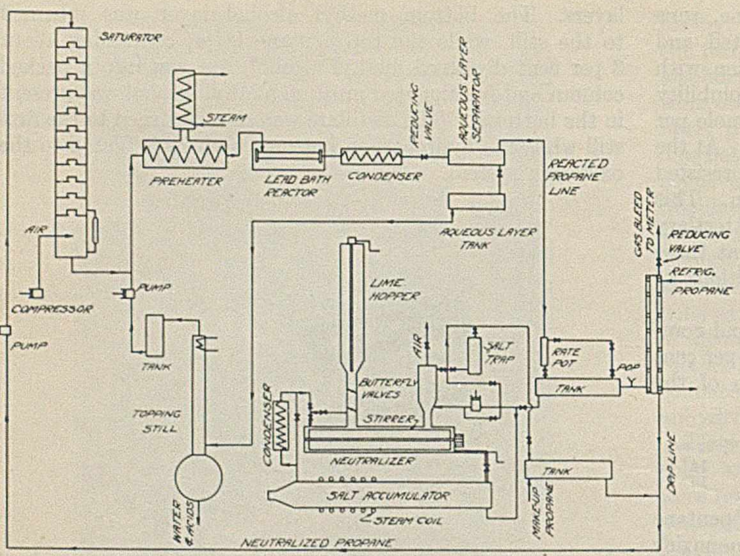


Figure 10. Flow Sheet for the Direct Oxidation of Propane to Acids

Discussion of Results

The fact seems to be established that the main useful oxidation product of methane at atmospheric pressure is formaldehyde. For instance, in the experiments of Layng and Soukoup (*48*) the products obtained showed a methyl alcohol–formaldehyde–formic acid relationship of about 1:8:3. The experiments of Bibb and Lucas (*8*) performed on a large scale showed a formaldehyde-methyl alcohol ratio of 5–1. Ledbury and Blair (*49*) also obtained formaldehyde as the chief product.

One factor which does not appear to have been taken into special consideration in most of the previous work is the purity of the hydrocarbon. Even so-called pure methane, especially that obtained from natural gas, is contaminated with small amounts of higher hydrocarbons which are removed only with considerable difficulty. In the present work the writers have encountered the same problem when working with a natural gas containing a few per cent of ethane. At pressures of about 200 atmospheres the main product obtained was methyl alcohol, and so the yields were calculated on the basis of methane reacting. However, in one case, a sample of methane was obtained from a different well, and appreciable amounts of ethyl alcohol were observed in the oxidation product. This led to an investigation which resulted in the conclusion that the reacting hydrocarbon in the previous cases was ethane, the reaction temperature of methane under those conditions being considerably higher than the temperature at which the runs were made. Since the amount of reaction per pass in this case was only about 2 to 5 per cent, all of the product may be readily accounted for by the presence of the impurity.

In the case of Bibb and Lucas' experiments (*8*) the gases contained as much as 7 per cent ethane; hence the methyl alcohol might have easily originated from the latter hydrocarbon. Furthermore, in a patent issued later (*6*), methyl alcohol was reported to be produced by the oxidation of ethane. The same impurities in the gases used by Layng and Soukoup (*48*) also may have been responsible to some extent for the methyl alcohol obtained in their experiments, although in this case the gas was recirculated until 27 per cent appeared as oxygenated products. The commercial process (*2, 90*) for the oxidation of natural gas to produce methyl alcohol and formaldehyde, mentioned by Egloff, Schaad, and Lowry (*24*), also operated with a gas rich in higher hydrocarbons. In this case, at 7 to 20 atmospheres pressure and 430° to 480° C., a 25 per cent ethane–75 per cent methane mixture yielded a product consisting of 4 per cent acetaldehyde, 60 per cent methyl alcohol, and 40 per cent formaldehyde. Patents granted later (*91*) indicated that under these conditions the methane was left substantially unaffected.

In the case of methane, the reaction for the formation of methyl alcohol involves the greatest decrease in volume and therefore should be favored most by increase in pressure. However, it must be remembered that the reaction for the complete oxidation of methane proceeds with a much greater decrease in free energy, so that even at high pressures it must be expected that a considerable amount of the reacting methane would be burned to carbon dioxide and water.

Above 300° C. both formaldehyde and methyl alcohol decompose according to the following reactions:

$$CH_2O \longrightarrow CO + H_2 \qquad (1)$$
$$CH_3OH \longrightarrow CO + 2H_2 \qquad (2)$$

Even at high total pressures, such decomposition would be possible because of the low partial pressures of these products in the reaction zone. Nevertheless, it can be predicted that reaction 2 would be suppressed by increase in pressure to a greater extent than reaction 1. This has been substantiated

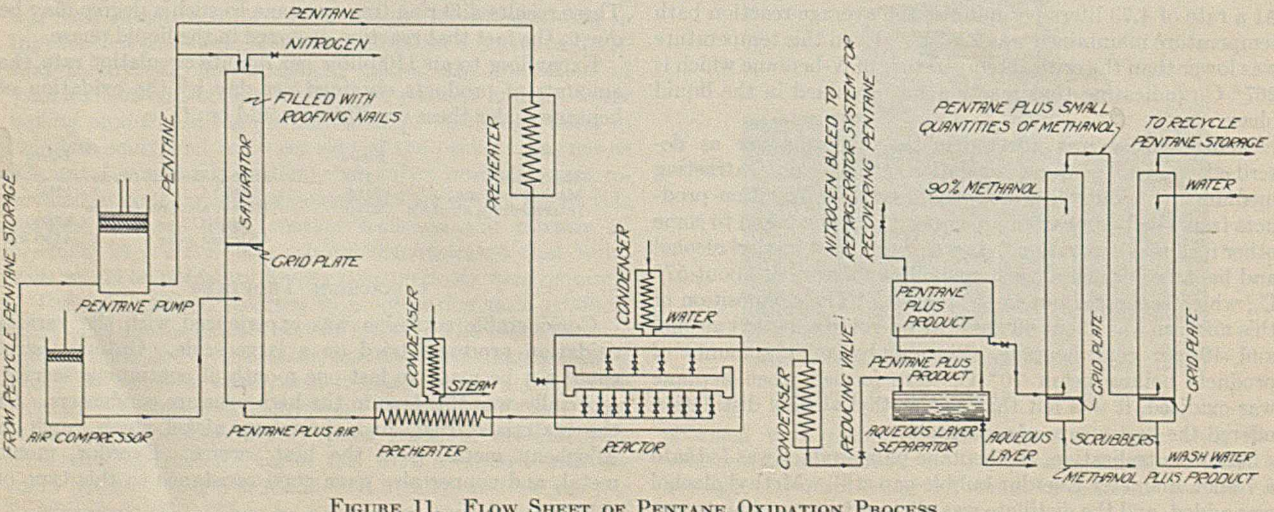


Figure 11. Flow Sheet of Pentane Oxidation Process

by high-pressure experiments on formaldehyde and methyl alcohol in which samples were submitted to conditions similar to those present during the runs. The approximate calculated values showed that at 260° C. about 2 per cent of the methyl alcohol was decomposed, and at 320° C. 4 per cent was decomposed; in the case of formaldehyde, the decomposition at 270° C. was about 3 per cent, at 310° it was 9 per cent, and at 340° the amount decomposed rose to 20 per cent. Likewise, it was shown that any carbon monoxide and hydrogen formed by thermal decomposition of the intermediate products may be further oxidized to carbon dioxide and water at the temperatures existing in the high-pressure runs.

A number of reaction mechanisms have been proposed as explanations for the complicated steps encountered during the process of oxidation (*4, 10, 11, 15, 24, 25, 50, 57, 59, 61, 87*). It is difficult to interpret the results obtained in the paper by any one of the existing theories. The data show that it is possible to produce methyl alcohol by the oxidation of methane at high pressure. This was also found to be the case recently by other investigators (*58, 60A*). Furthermore, oxidation of ethane yielded methyl alcohol as the main product, while propane gave a larger number of oxidized compounds. Pentane oxidation showed that rupture of the molecule likewise takes place, giving products of lower molecular weight. In the case of heptane, however, the reaction occurred in the liquid phase at a much lower temperature, and the products indicated that less degeneration to compounds of low molecular weight took place.

When oxidation is performed at relatively high temperatures, side reactions, such as dehydrogenation, cracking, and polymerization, will occur (*17, 29, 35, 60, 62, 71, 72, 76, 79, 81*) tending to complicate and conceal the initial oxidation reactions, thereby giving an opportunity for leading to unjustified conclusions (*70*). Consider, for instance, the case of a petroleum crankcase oil in an automobile. Under the operating conditions of the motor, there are at least four types of reactions which are capable of taking place in the presence of air:

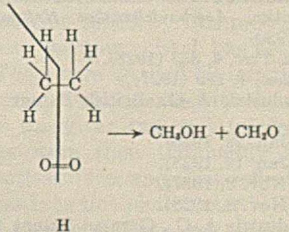
1. Cracking of the hydrocarbons may occur with simultaneous production of fixed gases and olefins.
2. Direct oxidation of paraffin hydrocarbons or paraffinic groups may take place resulting in the formation of oxygen containing products such as acids, aldehydes, etc., capable of polymerizing to materials known as sludge.
3. Dehydrogenation of hydrocarbons, particularly of the heavy naphthenes, can be brought about by oxygen, giving water, olefinic compounds, asphaltenes, and other sludge-forming ingredients.
4. The olefins produced by these means, or even those present in the original oil, may be caused to polymerize by the initiating effect of the oxygen, to produce higher boiling hydrocarbons. Some direct oxidation of the olefins is also liable to take place. Furthermore, if some ozone is present, ozonides will be formed with possible production of aldehydes, ketones, and their polymerization products.

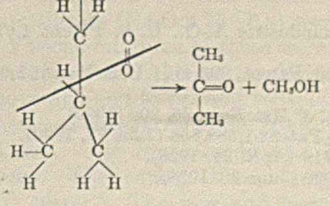
Therefore, unless one is dealing with a pure hydrocarbon, oxidized under such conditions that no other interfering reactions are capable of taking place, one has an exceedingly difficult task in explaining the mechanism involved.

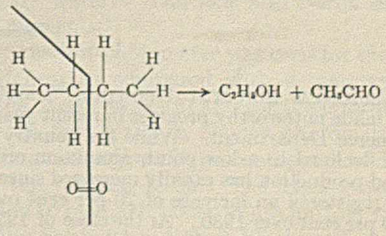
As has been shown in this paper, when pressure is applied, the temperature at which appreciable oxidation takes place is lowered considerably, the extent depending upon the pressure, so that excessive temperatures are not required for carrying on oxidations at high pressures. When the whole homologous series of saturated paraffin hydrocarbons is considered, the striking feature which can be noted is the great difference in reaction temperatures of the individual members (*29*). Although the hydrocarbons of low molecular weight, such as methane, ethane, and propane, possess exceptionally high stability, necessitating reaction with oxygen in the vapor state at high temperatures (even at high pressures), the homologs of higher molecular weight are relatively unstable, reacting easily at low temperatures in the liquid phase.

The types of compounds formed in the present experiments would be determined, according to probability, by the number of impacts of oxygen molecules upon the hydrocarbon molecule, by the relative strengths of the bonds under the given conditions, as well as by the location of the reacting molecules when the reaction temperature is reached. For instance, the longer the hydrocarbon molecule, the greater would be the number of individual products formed and the greater would be the probability of attack at different points of the same hydrocarbon molecule. Likewise, the longer the time of contact of the hydrocarbon with oxygen, the greater would be the chances of attack on other portions of the molecule and further oxidation of oxidation products already formed. In the case of the lower hydrocarbons, the high temperature required for reaction and the small sizes of the reacting molecules result in the production of products of low molecular weight, whereas the oxidation of wax (generally taken as 24 carbon atoms) at the lowest reaction temperature involves the formation of products equally distributed from 1 to 24 carbon atoms, the average molecular weight ranging at about 14 carbon atoms. Also considerable amounts of hydroxy and keto compounds are produced (*1, 16, 31, 32, 36, 47*). The structure of the hydrocarbon also plays an important role with respect to the ease of oxidation. For instance, Pope, Dykstra, and Edgar (*61*) have found that the straight-chain octane reacts readily with oxygen while 2,2,4-trimethylpentane is so stable to oxidation that no reaction occurs at atmospheric pressure until such a high temperature is reached that reaction, once started, goes rapidly to completion.

In all these cases, scission of the carbon-hydrogen bond appears to occur simultaneously with the oxidation. This would be expected since the carbon-carbon bond in general is weaker than the carbon-hydrogen bond (*62*). The over-all reaction in the case of the hydrocarbons discussed in this paper might be expressed as follows:







Acknowledgment

The laboratory data reported are the outcome of investigations conducted by the writers and their associates several

years ago in the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology.

The writers wish to acknowledge their indebtedness to S. P. Coleman of the Humble Oil & Refining Company and to R. E. Tannich and J. M. Whiteley at that time connected with the Breckenridge Plant of that company, as well as to W. K. Lewis of the Massachusetts Institute of Technology and H. E. Buc of the Standard Oil Development Company.

Literature Cited

(1) Alox Chemical Corp., French Patent 672,813 (April 8, 1928).
(2) Anonymous, *Chem. Eng. Catalog Bull.* 123 (1928).
(3) Assoc. Official Agr. Chem., Methods of Analysis, p. 137 (1925).
(4) Bates and Spence, *J. Am. Chem. Soc.*, 53, 1689 (1931).
(5) Bermejo, *Anales soc. españ. fís. quím.*, 27, 695 (1929).
(6) Bibb, Canadian Patent 302,672 (Jan. 29, 1930).
(7) Bibb, U. S. Patent Reissue 15,789 (March 11, 1924).
(8) Bibb and Lucas, Ind. Eng. Chem., 20, 1152 (1928).
(9) Bitler and James, *Chem. & Met. Eng.*, 35, 156 (1928).
(10) Bone and Andrew, *J. Chem. Soc.*, 87, 1232 (1905).
(11) Bone and Drugman, *Proc. Chem. Soc.*, 20, 127 (1924).
(12) Boomer, U. S. Patent 1,776,771 (July 23, 1928).
(13) Bostaph Eng. Co. (from Ramage), U. S. Patent 1,224,787 (May 1, 1917).
(14) Brooks, *J. Inst. Petroleum Tech.*, 14, 744 (1928).
(15) Brunner and Rideal, *J. Chem. Soc.*, 1928, 1162.
(16) Burwell, U. S. Patents 1,690,768-69; 1,770,875-76 (Dec. 20, 1926).
(17) Carbide and Carbon Chemicals Corp., British Patent 238,938 (May 26, 1924).
(18) Carman, U. S. Patent 1,697,105 (Jan. 1, 1929).
(19) Carman and Chilton, U. S. Patent 1,697,106 (Jan. 1, 1929).
(20) Cooper and Wiezevich, Ind. Eng. Chem., 21, 1210 (1929).
(21) Darrah, U. S. Patent 1,448,655 (March 13, 1923).
(22) Dyer, *J. Biol. Chem.*, 28, 445 (1917).
(23) Egloff and Schaad, *Chem. Rev.*, 6, 91 (1929).
(24) Egloff, Schaad, and Lowry, Ind. Eng. Chem., 21, 785 (1929).
(25) Elsworthy, *Trans. Roy. Soc. Can.*, III, 16, 93 (1922).
(26) Fort and Hinshelwood, *Proc. Roy. Soc.* (London), A129, 296 (1930).
(27) Frolich, Ind. Eng. Chem., 23, 111 (1931).
(28) Frolich, Harrington, and Waitt, *J. Am. Chem. Soc.*, 50, 3216 (1928).
(29) Frolich and Wiezevich, Ind. Eng. Chem., 24, 13 (1932).
(30) Gillespie and Walters, *J. Am. Chem. Soc.*, 39, 2027 (1917).
(31) Gutt and Plotko, *Azerbaidzhanskoe Neftyanoe Khozyaistvo*, No. 9, 108 (1930).
(32) Hebler, *Erdöl u. Teer*, 4, 333 (1928).
(33) Henri, *Chem. Rev.*, 4, 189 (1927).
(34) I. G. Farbenindustrie A.-G., British Patent 199,886 (May 2, 1922).
(35) *Ibid.*, 265,234 (Jan. 29, 1926).
(36) *Ibid.*, 304,150 (Jan. 14, 1928).
(37) *Ibid.*, 304,855 (Nov. 2, 1927).
(38) *Ibid.*, 325,234 (Nov. 8, 1928).
(39) I. G. Farbenindustrie A.-G., German Patent 408,184 (July 28, 1920).
(40) I. G. Farbenindustrie A.-G., U. S. Patent 1,677,730 (July 2, 1925).
(41) Jaeger, British Patent, 291,419; U. S. Patent 1,907,853 (June 3, 1927).
(42) James, *Chem. & Met. Eng.*, 26, 209 (1922).
(43) James, U. S. Patent 1,588,856 (June 15, 1926).
(44) *Ibid.*, 1,667,419 (April 24, 1928).
(45) *Ibid.*, 1,675,029 (June 26, 1928).
(46) Kloppenburg (to Naamlooze Vennotschap Bataafsche Petroleum Maatschappij), U. S. Patent 1,500,080 (July 26, 1922).
(47) Landa, Ind. Eng. Chem., News Ed., 6, 9 (1928).
(48) Layng and Soukoup, Ind. Eng. Chem., 20, 1152 (1928).
(49) Ledbury and Blair, Dept. Sci. Ind. Research, *Special Rept.* 1 (1927).
(50) Lind and Bardwell, *J. Am. Chem. Soc.*, 48, 2335 (1926).
(51) Lucius and Bruning, German Patent 382,391 (May 18, 1921).
(52) Medvedev, *Chimie & industrie*, 18, 997 (1927); *Trans. Karpov Chem. Inst.*, No. 126 (1926).
(53) Medvedev, Russian Patent Application 3605 (Sept. 30, 1927).
(54) Medvedev, *Trans. Karpov Chem. Inst.*, No. 3, 54 (1924).
(55) Medvedev and Robinson, *Ibid.*, No. 4, 117 (1925).
(56) Minerals Separation North American Corp. (from Martin), U. S. Patent 1,678,403 (Oct. 30, 1920).
(57) Mondain-Monval and Quanquin, *Compt. rend.*, 191, 299 (1930).
(58) Newitt and Haffner, *Proc. Roy. Soc.* (London), A134, 591 (1932).
(58A) Newitt and Townend, *Petroleum Times*, 30, 140 (1933).
(59) Pease, *J. Am. Chem. Soc.*, 51, 1855 (1929).
(60) Penniman, British Patent 252,337 (May 20, 1925).
(60A) Pichler and Reder, *Z. angew. Chem.*, 46, 161 (1933).
(61) Pope, Dykstra, and Edgar, *J. Am. Chem. Soc.*, 51, 1875, 2203 (1929).
(62) Ramage (to Bostaph Eng. Co.), U. S. Patent 1,678,078 (June 19, 1925).
(63) Randowsky, *Chem. Zentr.*, 1928, II, 218.
(64) Rice, *J. Am. Chem. Soc.*, 53, 1959 (1931).
(65) Roelen, *Ges. Abhandl. Kenntnis Kohle*, 7, 11 (1925); *Chem. Zentr.*, 1926, II, 1398.
(66) Ryerson and Swearigan, *J. Phys. Chem.*, 32, 192 (1928).
(67) Schönfelder, *Ber. Ges. Kohlentechnik, IV*, 247 (1923); *J. Inst. Petroleum Tech.*, 10, 35A (1924); *Fuel*, 4, 547 (1925).
(68) Schönfelder, *J. Chem. Soc.*, 124, 1, 1175 (1923).
(69) Smith and Milner, Ind. Eng. Chem., 23, 357 (1931).
(70) Spindler, French Patent 637,050 (Jan. 23, 1928).
(71) Standard Oil Development Co., British Patent 321,494 (Sept. 7, 1931).
(72) Standard Oil Development Co. (from Hopkins), Canadian Patent 264,192 (May 21, 1924).
(73) *Ibid.* (from Howard), 267,743 (May 15, 1924).
(74) *Ibid.* (from Loomis), 267,745 (May 30, 1924).
(75) *Ibid.* (from Lewis and Frolich), 289,856 (1929).
(76) Standard Oil Development Co., French Patent 660,825 (Sept. 22, 1928).
(77) *Ibid.*, 682,979 (Oct. 29, 1929).
(78) Standard Oil Development Co. (from Young), U. S. Patent 1,735,486 (Aug. 4, 1928).
(79) *Ibid.* (from Howard), 1,758,898 (May 13, 1930).
(80) *Ibid.* (from Hopkins), 1,767,363 (Aug. 16, 1922).
(81) *Ibid.* (from Hopkins), 1,808,168 (June 24, 1930).
(82) *Ibid.* (from Pugh, Tauch, and Warren), 1,812,714 (Aug. 4, 1928).
(83) *Ibid.* (from Buc), 1,820,907 (Sept. 1, 1931).
(84) *Ibid.* (from Wiezevich and Tannich), 1,838,032 (Sept. 12, 1929).
(85) *Ibid.* (from Frolich), 1,858,822 (Oct. 14, 1927).
(86) *Ibid.* (from Lewis), 1,870,816 (Jan. 26, 1928).
(87) Stephens, *J. Am. Chem. Soc.*, 50, 2523 (1928).
(88) Trautz and Schleuter, *Z. anorg. allgem. Chem.*, 136, 1 (1924).
(89) Upson, Plum, and Schott, *J. Am. Chem. Soc.*, 39, 731 (1917).
(90) Walker (to Empire Fuel & Gas Co.), British Patent 290,613; French Patent 657,383 (May 17, 1927).
(91) Walker (to Empire Fuel & Gas Co.), British Patent 295,356; French Patent 657,394 (Aug. 10, 1927).
(92) Walter, British Patent 21,941 (not granted) (Oct. 27, 1904).
(93) Wieland, *Ber.*, 45, 493 (1912).

Received September 23, 1933.

Italy's Aluminum Industry Growing. Italy's aluminum industry has made noteworthy progress in recent years, according to the Commerce Department. While the country's copper resources have declined to a low point, aluminum ores have been developed and production has rapidly increased since 1926. The 1932 output registered an increase of 20 per cent over 1931 and more than 70 per cent over 1930. At the close of 1932, Italy had attained sixth place among the world's aluminum-producing nations, the countries which outranked her being, in the order of their importance, the United States, Germany, Canada, Norway, and France. Progress in the Italian industry has been favored by extensive and low-priced hydroelectric power.

Prior to 1929 there were only two aluminum factories in Italy. The augmented production during and since 1929 resulted from the opening of two modern plants in that year, the combined potential output of which is approximately 10,000 metric tons. There are four plants in the country manufacturing aluminum metal in the form of ingots, bars, castings, plates, wires, and tubes, the industry giving employment to about 2000 workers.

Because of the large world production of aluminum metal, Italian production in 1933 was substantially curtailed. The excess of production over domestic demand is approximately 60 per cent, a situation which constitutes one of the problems of the industry. A partial solution was found in 1933 by opening up a new market in Japan. Russia also provided a favorable outlet.

The Value of Silicate of Soda as a Detergent

III. Siliceous Silicate in Water Containing Either Calcium Bicarbonate or Carbon Dioxide

John D. Carter and William Stericker, Philadelphia Quartz Co., Philadelphia, Pa.

The ability of sodium oleate to remove dirt from cotton cloth and to prevent its redeposition on clean cloth is decreased by the presence of calcium bicarbonate in the wash water. Mixtures of sodium silicate ($Na_2O:3.25SiO_2$) and this soap are less affected by the calcium salt and become equal to or better than soap alone. Since the pH of the solutions is below 10.2, they may be considered acid to soap, but they have marked detergent properties. Carbon dioxide alone does not have as much effect on sodium oleate as calcium bicarbonate. The addition of the sodium silicate largely neutralizes the effects due to carbon dioxide.

IN THE second paper (*2*) of this series[1] it was shown that sodium silicates largely prevented the deposition of dirt or pigments from water suspensions on to cloth while other alkaline builders, except trisodium phosphate, did not. The phosphate was not nearly as effective as the silicates. This deposition was shown to be a factor in washing because solid dirt was removed from one piece of cloth and deposited on another in the same detergent solution. As would be expected, soap had marked ability to remove dirt and prevent it from being redeposited, but mixtures of soap and silicates were as good or better than either alone with siliceous soils and pigments.

All the work reported in the preceding paper was with distilled water. In actual laundry practice, whether at home or in the power laundry, the water is either naturally hard or softened. The softening may be done by either the zeolite or the lime-soda process. The experiments described in this and subsequent papers were undertaken to discover what effect some of the constituents of such waters might have on the removal and redeposition of dirt.

Experimental Methods

The results of two series of experiments are included. In the first series, half the strip of Utica sheeting was soiled with a mixture containing 0.6 gram gum tragacanth, 10 grams wheat starch, 20 grams pigment (except carbon black, of which only 5 grams were used), and 250 grams water. The other half was left unsoiled and a clean strip of sheeting was placed in a jar with the partially soiled strip. The washing was done in the launderometer for 20 minutes at 60° C. with ten rubber balls and 100 ml. of detergent solution made from the water being tested. There were then two rinses of 5 minutes each with 100 ml. of the same water. The samples were dried and compared after four, nine, fourteen, and twenty cycles, and finally the reflecting power was measured in a Hess-Ives tint photometer.

This series indicated that the conclusions drawn about the effectiveness of various detergents in removing dirt were not changed with an increased number of washes. Since the additional washes took a great deal of time and the samples which resulted were harder to evaluate, it appeared desirable to decrease the number of washes. Burkhart and Falkman (*1*) have shown that the shorter method leads to the same conclusions as the longer with a simple pigment soil. With fewer washes it is much easier to judge the degree of protection, since pigments which are deposited in the early washes are washed out again in the later ones. In the second series, undertaken later, the maximum number of washes was five.

In the second series, pieces of Utica sheeting (7.6 by 12.7 cm.) were made into bags, each containing fifty monel metal balls 0.25 inch (0.635 cm.) in diameter. To soil these bags they were placed in a jar in the launderometer with a suspension of 1 gram of the pigment (except carbon black, of which only 0.25 gram was used) in 100 ml. of distilled water and rotated for 20 minutes at 60° C. The bag was then removed and rinsed with tap water (Philadelphia's Delaware River supply) until no more pigment was removed. This is a method which has been tried by the Detergents Committee of the American Oil Chemists Society and has been found to give satisfactory soiling (*5*). The bags were then cut open and dried on a smooth surface.

The washing tests themselves were made by placing one bag made of sheeting soiled by this method in a jar with a bag made of clean sheeting. Each bag contained fifty monel metal balls. They were washed 20 minutes at 60° C. with 100 ml. of detergent solution made with the water being tested, One set of bags was given two such treatments and another five. The bags were then thoroughly rinsed, cut open, dried on a smooth surface, and their reflecting powers measured with a Hess-Ives tint photometer.

Solutions containing 0.2 per cent sodium oleate and 0.2 per cent sodium silicate ($Na_2O:3.25\ SiO_2$) were made up with each water. Various mixtures of these were compared with the original solutions and the water alone, both for their ability to remove dirt and to prevent redeposition.

The pigments used were ferric oxide, raw and burnt umbers, and carbon black. The ferric oxide was Merck's ignited rouge or crocus. The carbon black was extracted and readily wet by water.[2] The raw and burnt umbers were commercial pigments.[3]

The Hess-Ives tint photometer was used for the determination of whiteness as compared with a standard magnesia block. In the earlier work (*2*) and for the intermediate comparisons in the first series, a Taylor photometer was used and the readings were given in percentages of whiteness compared with the original cloth. The Hess-Ives instrument has been found to be much easier to use for this work. Comparison of the figures for carbon black and raw umber in distilled water shows that the conclusions drawn would not be greatly altered whichever instrument was used (Figure 1),

---

[1] Part I appeared in Ind. Eng. Chem., 15, 244 (1923).

[2] Grade J obtained from L. Martin Company, Philadelphia.

[3] Obtained from Eugene E. Nice Company, Philadelphia.

Table I. Reflecting Power of Sheeting Soiled with Various Agents and Washed in Distilled Water

(In percentages of whiteness, magnesia block standard)

Cloth soiled with:	Carbon Black			Burnt Umber			Raw Umber			Ferric Oxide		
No. of washes:	2	5	20	2	5	20	2	5	20	2	5	20
(A) Water	38.5	45.3	46.2	28.1	35.8	41.6	32.8	41.7	40.3	41.6	53.0	45.1
(B) 0.2% soln. of $Na_2O:3.25SiO_2$	36.5	48.6	65.5	36.7	48.2	47.7	44.5	57.8	56.2	51.6	65.6	56.1
(C) 4 parts of silicate with 1 of soap soln.	40.4	50.7	69.7	41.6	55.7	54.4	47.5	62.8	54.3	63.8	75.2	65.2
(D) Equal parts of silicate and soap soln.	38.7	50.7	..	37.5	59.9	..	49.4	58.7	..	61.2	73.8	..
(E) 1 part of silicate with 2 of soap soln.	..	..	70.6	..	..	56.4	..	..	54.9	..	..	71.8
(F) 1 part of silicate with 4 of soap soln.	36.1	53.4	..	43.4	62.0	..	54.0	69.8	..	68.3	83.5	..
(G) 0.2% soln. of sodium oleate	45.8	54.1	68.9	45.1	60.1	60.1	55.5	66.7	62.3	64.4	78.7	76.5
PROTECTION OF CLOTH ORIGINALLY UNSOILED												
(A) Water	57.2	64.5	61.8	43.8	57.3	62.3	58.3	62.4	68.3	56.8	59.4	56.0
(B) Silicate	60.2	73.9	75.7	62.2	77.4	80.6	68.5	83.6	86.9	65.9	75.5	74.5
(C) 4 silicate, 1 soap	65.6	73.9	87.4	77.8	91.1	90.1	85.7	94.7	90.5	79.3	87.1	87.2
(D) Equal silicate and soap	70.0	77.9	..	85.2	90.8	..	88.2	96.4	..	86.5	89.4	..
(E) 1 silicate, 2 soap	..	..	89.1	..	..	94.3	..	..	89.8	..	..	90.8
(F) 1 silicate, 4 soap	70.3	78.3	..	85.4	96.7	..	91.5	96.2	..	89.0	87.1	..
(G) Soap	70.5	77.5	78.3	84.2	95.7	89.0	92.1	95.5	90.5	86.3	90.5	93.4

Table II. Reflecting Power of Sheeting Soiled with Various Agents and Washed in Water Containing Calcium Carbonate and Carbon Dioxide

(In percentages of whiteness, magnesia block standard)

Cloth soiled with:	Carbon Black			Burnt Umber			Raw Umber				Ferric Oxide		
No. of washes:	2	5	20	2	5	20	2	5	5	20	2	5	20
(A) Water	31.8	37.8	41.0	25.1	33.4	37.6	29.7	34.4	34.9	43.7	37.1	39.4	48.4
(B) 0.2% soln. of $Na_2O:3.25SiO_2$	34.3	46.1	46.0	34.3	47.4	47.6	38.1	54.9	55.9	50.8	45.5	57.5	50.4
(C) 4 parts of silicate with 1 of soap soln.	37.3	51.0	49.0	38.1	51.9	52.1	40.7	55.9	56.8	58.6	46.3	64.5	53.7
(D) Equal parts of silicate and soap soln.	37.1	51.8	..	38.9	54.6	..	44.5	62.8	62.3	..	50.7	62.8	..
(E) 1 part of silicate with 2 of soap	..	..	49.0	..	..	58.2	..	..	..	57.9	..	..	55.0
(F) 1 part of silicate with 4 of soap	40.3	54.3	..	39.5	56.6	..	44.4	63.9	64.2	..	44.6	53.1	..
(G) 0.2% soln. of sodium oleate	38.2	51.8	46.0	39.9	39.8	49.8	44.0	52.5	54.7	52.0	40.5	48.5	55.9
PROTECTION OF CLOTH ORIGINALLY UNSOILED													
(A) Water	45.7	52.6	58.0	44.5	46.3	58.9	51.0	51.3	51.2	63.9	50.2	50.4	56.2
(B) Silicate	53.4	65.3	68.0	52.2	64.9	76.3	60.4	73.8	73.0	77.8	56.4	68.7	62.0
(C) 4 silicate, 1 soap	55.3	69.5	68.0	65.8	74.6	78.5	71.7	83.3	82.7	79.8	60.7	77.2	63.1
(D) Equal silicate and soap	64.8	78.9	..	78.1	88.5	..	81.2	92.7	92.4	..	65.0	77.8	..
(E) 1 silicate, 2 soap	..	..	71.8	..	..	79.1	..	..	..	77.6	..	..	64.8
(F) 1 silicate, 4 soap	69.6	78.0	..	80.9	89.7	..	87.5	92.9	94.2	..	61.6	73.0	..
(G) Soap	65.5	73.5	58.2	77.3	74.4	60.8	87.6	89.5	89.1	63.9	60.1	66.7	54.9

but small differences are more easily read with the Hess-Ives instrument because of its greater accuracy.

The original sheeting was 90.9 per cent white. Average figures for the soiled cloth in the second series were as follows: carbon black, 24.4 per cent; burnt umber, 19.5; raw umber, 24.9; and ferric oxide, 26.5.

Distilled Water

The results with distilled water in each series are included as a basis for comparison. Because of differences in the method of soiling and washing in the two series, the results given in Table I are not in entire agreement. In the first series of twenty washes the addition of silicate to the water increased the removal of all four pigments. The addition of soap alone to the water caused greater removal than that effected by the silicate. When mixtures of soap and silicate were used, the results with burnt umber and ferric oxide were intermediate between those with either detergent alone, and with carbon black were better than with either alone. The mixtures were less effective with raw umber. In the second series the results with two suds were more erratic than those with five but, in general, agree with them. Burkhart and Falkman (*1*) have found that a certain minimum number of washes was necessary before discrepancies disappeared. For that reason, the results with five suds will be used in drawing conclusions. Again, sodium silicate showed that it had detergent powers but that they were not as great as those of soap. The mixture of four parts of soap and one of silicate removed more of the umbers and ferric oxide than soap alone. With carbon black there was practically no difference. The other mixtures were less effective than soap alone but more so than sodium silicate alone.

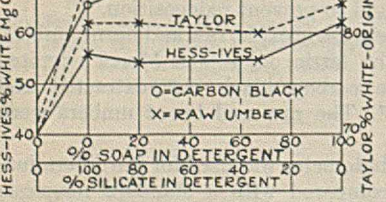


Figure 1. Comparison of Whiteness Readings with Taylor and Hess-Ives Instruments

In the first series the maximum protection of the clean cloth was obtained with soap alone when ferric oxide (and raw umber) was the soil and with two-thirds soap and one-third silicate on carbon black and burnt umber. In the second series there was very little difference between soap alone and the mixtures.

Calcium Bicarbonate

A common constituent of hard water is calcium bicarbonate. In order to determine its effect on the removal and redeposition of dirt, a solution was prepared by suspending 1.53 grams of calcium carbonate in 18 liters of distilled water and adding gaseous carbon dioxide until all the carbonate dissolved on standing overnight. The hardness of the resulting solution was equivalent to 85.7 parts per million (5 grains per gallon) of calcium carbonate and its pH was 5.6 (bromocresol purple). In the first series this solution was used for both the suds and rinses, but in the second the rinses were with distilled water. With soap a very turbid solution was produced but no visible curds formed, and there was no precipitation even after standing several days. The silicate solution was nearly clear.

The results are given in Table II. It is evident that, in general, the calcium bicarbonate has prevented removal and increased redeposition. The effect on soap alone is greater than on silicate alone or on silicated soap. For example, cloth soiled with burnt umber and washed with soap five times dropped from 60 per cent when distilled water was used to 40 per cent whiteness when the bicarbonate was present; under the same conditions a mixture of 80 per cent soap and 20 per cent silicate went only from 56 to 52 per cent. Some idea of the differences can be obtained by comparing Figure 2*a* with 2*b*,[4] or Figures 3*a* and 3*d* with 3*b* and 3*e*, respectively.[4] Since the silicate-soap mixtures are less affected by the hardness, they become equal to or better than soap alone for the removal of dirt. In every case except one (two washes, raw umber) they were superior in preventing redeposition.

Accidentally in this series of experiments the raw umber samples with five washes were duplicated. Figures for both sets of samples are given to show how close the agreement was (Table II).

When the detergent solutions used in the second series were prepared, their pH's were determined as shown in Table III.

TABLE III. pH OF DETERGENT SOLUTIONS WITH CALCIUM BICARBONATE

DETERGENT SOLUTION	pH	CALCIUM BICARBONATE INDICATOR
Water alone	5.6	Bromocresol purple
Soap	6.2	Bromocresol purple
80% soap, 20% silicate	6.5	Bromocresol purple
50% soap, 50% silicate	8.4	Phenol red
20% soap, 80% silicate	9.0	Thymol blue
Silicate	9.6	Thymol blue

Only a glance at the results is necessary to show that neither removal nor protection is proportional to the pH within the range studied. The low values, especially for the first three in Table III, do raise the question of whether the formation

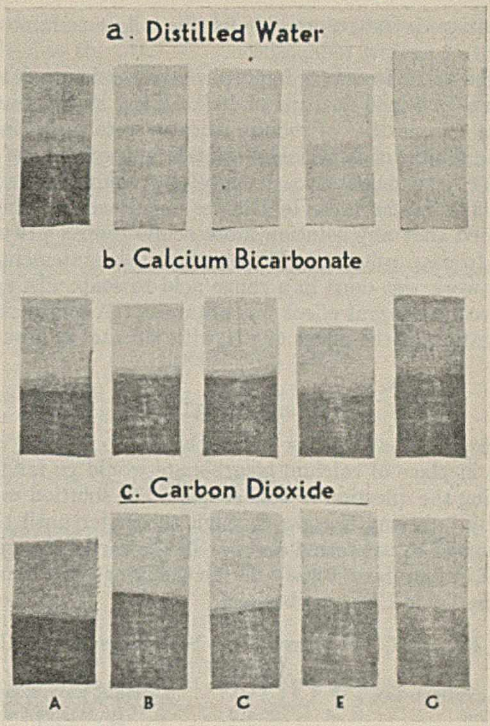


FIGURE 2

a. Strips given twenty washes with distilled water; lower portions were originally soiled with carbon black while upper portions were clean; letters refer to solutions described in Table I.

b. Strips given twenty washes with water containing calcium bicarbonate and rinsed with same; soiled with carbon black as in 2*a*; samples *E* and *G* were yellower when this picture was taken than they were immediately after washing; figures given in Table II.

c. Strips given twenty washes with water containing carbon dioxide and rinsed with same; soiled with carbon black; figures given in Table V.

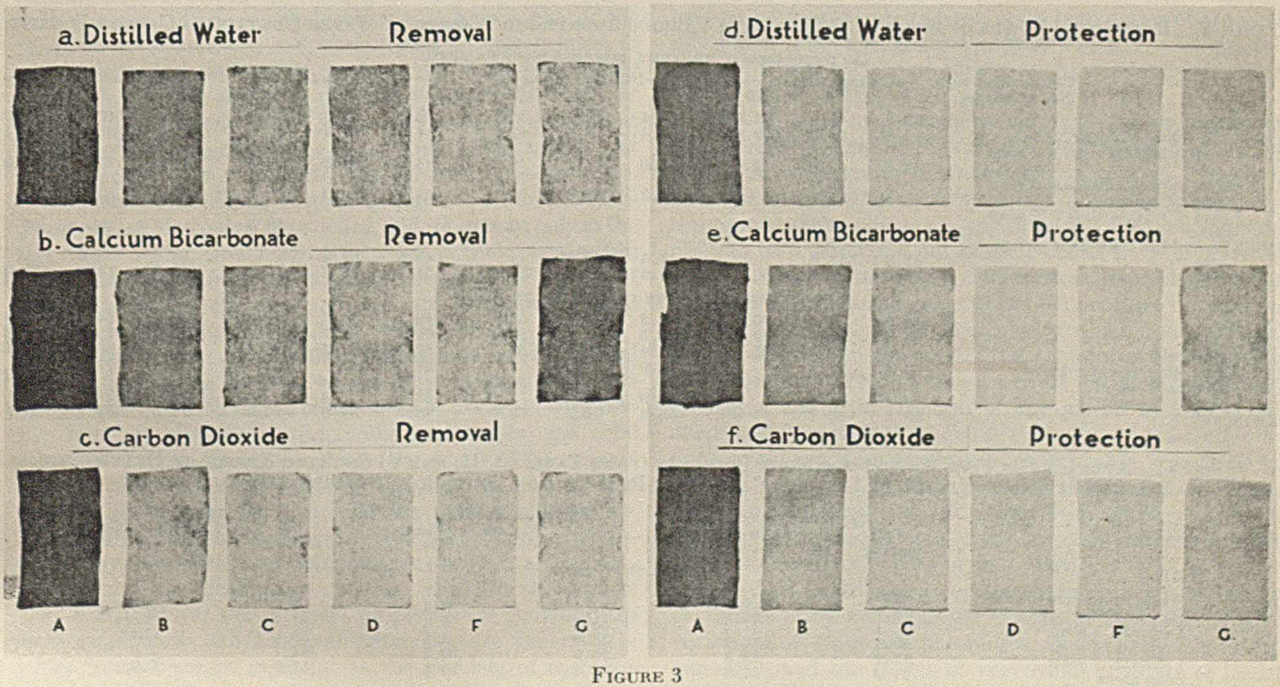


FIGURE 3

a. Strips soiled with burnt umber; washed five times in distilled water (Table I).

b. Strips soiled with burnt umber; washed five times in water containing calcium bicarbonate (Table II).

c. Strips soiled with burnt umber; washed five times in water containing carbon dioxide (Table V).

d. Clean strips washed five times with strips shown in 3*a*.

e. Clean strips washed five times with those shown in 3*b*.

f. Clean strips washed five times with those shown in 3*c*.

(The capital letters refer to the corresponding solutions given in Table II.)

---

[4] The samples washed with soap in hard water in the first series had turned yellow to some extent before the photographs were taken. This makes the contrast more striking than when the original readings were made. No such action took place in the second series where distilled water was used in rinsing.

of acid soaps is not responsible for the failure to remove dirt and protect against redeposition.

Rhodes and Bascom (*3*) found that the maximum detergent effect was obtained at a pH of 10.7. They stated, however, that the complexities of sodium silicates were such that they were the subject of a special investigation, the results of which have not been published. None of the solutions used here was as alkaline as those of Rhodes and Bascom. Snell (*4*) has stated that any solution more acidic than a pH of 10.2 is acid to soap solution. If we accept this statement, then all this work was done in a range acid to soap. In spite of this, a real detergent effect was obtained. A more extended investigation of the effect of pH with silicates is now under way.

CARBON DIOXIDE

It was felt that the use of a solution containing carbon dioxide in place of calcium bicarbonate would go far toward answering the question of acid soaps. The solution was prepared by bubbling the gas through the water until the pH had dropped to between 4 and 5. In the earlier experiments with the strips, the pH was 4.6. In the later series the values shown in Table IV were obtained.

TABLE IV. PH OF DETERGENT SOLUTIONS WITH CARBON DIOXIDE

DETERGENT SOLUTION	PH	CARBON DIOXIDE INDICATOR
Water alone	4.3	Bromocresol green
Soap	7.6	Phenol red
80% soap, 20% silicate	8.4	Thymol blue
50% soap, 50% silicate	9.6	Thymol blue
20% soap, 80% silicate	9.9	Nitro yellow
Silicate	10.0	Nitro yellow

Even though the initial pH was lower, the figures for the solutions of soap and silicate were higher than with the bicarbonate. This was without doubt due to the precipitation of calcium soap or/and silicate, leaving sodium bicarbonate in solution which contained less active alkali to raise the pH.

Five suds with mixtures of soap and silicate in the presence of carbon dioxide removed more of the pigments than five suds with either detergent alone (Table V). The same was true with two suds, except raw umber which was an exception in that soap removed it best. The optimum mixture varies, but with five suds, the cleanest cloth was obtained three times with equal parts of soap and silicate and once with four parts of soap to one of silicate. With twenty washes, in the presence of gum tragacanth and starch, soap alone gave the cleanest cloth although silicate and silicate-soap mixtures were equally good with carbon black.

The best protection with two or five suds was given by the mixture containing four parts of soap and one of silicate. In the earlier series of twenty washes the best protection, except with ferric oxide, was with four parts of silicate and one of soap; the least ferric oxide was deposited with soap alone.

Table VI shows the average results with the series given five washes. With no detergent, with soap alone, or with a mixture of four parts of soap with one of silicate, the presence of carbon dioxide decreases the amount of dirt removed but not as greatly as the presence of calcium bicarbonate. In general, the results with two and five washes confirm this. With silicate alone or with mixtures containing more silicate than the one given above, carbon dioxide either has no effect or, apparently, a beneficial one (Figure 2*c* compared with 2*a* and 2*b*, and Figure 3*d* with 3*a* and 3*b*).

In spite of the smaller amounts of dirt removed and therefore available for redeposition, the amount deposited from water containing carbon dioxide is greater than from distilled water but not as great as from water containing calcium bicarbonate (Figure 2*c* compared with 2*a* and 2*b* and Figure 3*f* with 3*d* and 3*e*).

These results indicate that the formation of acid soaps probably is a partial explanation of the adverse effect of calcium bicarbonate but not the entire one. The formation of insoluble calcium oleate and silicates with the correspond-

TABLE V. REFLECTING POWER OF SHEETING SOILED WITH VARIOUS AGENTS AND WASHED IN WATER CONTAINING CARBON DIOXIDE

(In percentages of whiteness, magnesia block standard)

Cloth soiled with:	CARBON BLACK			BURNT UMBER			RAW UMBER			FERRIC OXIDE		
No. of washes:	2	5	20	2	5	20	2	5	20	2	5	20
(A) Water	35.7	41.0	46.0	24.4	29.9	38.7	29.8	37.2	39.3	40.6	47.2	41.6
(B) 0.2% soln. of Na_2O:3.25SiO_2	39.8	46.6	59.0	36.4	50.1	43.3	44.3	59.4	57.6	49.6	67.0	52.1
(C) 4 parts of silicate with 1 of soap soln.	44.7	47.8	59.0	40.0	51.7	46.2	44.6	66.3	59.6	61.0	78.7	55.9
(D) Equal parts of silicate and soap soln.	42.3	54.7	..	41.2	53.3	..	48.3	70.0	..	59.1	82.1	..
(E) 1 part of silicate with 2 of soap soln.	..	..	60.0	..	..	50.3	..	..	58.5	..	..	58.2
(F) 1 part of silicate with 4 of soap soln.	41.8	53.6	..	41.4	59.4	..	49.6	67.8	..	56.2	78.0	..
(G) 0.2% soln. of sodium oleate	38.6	50.6	60.0	32.6	52.0	56.5	51.9	54.2	71.5	56.6	74.7	76.3
PROTECTION OF CLOTH ORIGINALLY UNSOILED												
(A) Water	53.6	56.6	70.0	43.3	49.1	66.3	49.1	51.0	63.3	53.5	55.3	48.1
(B) Silicate	58.6	70.8	79.0	57.5	78.0	83.4	66.9	80.7	83.1	63.4	78.9	62.4
(C) 4 silicate, 1 soap	61.3	72.3	85.0	72.4	87.3	88.5	82.4	92.7	91.4	75.8	88.0	65.2
(D) Equal silicate and soap	64.8	74.9	..	77.0	90.2	..	87.4	92.7	..	77.8	91.3	..
(E) 1 silicate, 2 soap	..	..	82.0	..	..	80.4	..	..	86.8	..	..	70.4
(F) 1 silicate, 4 soap	67.8	82.0	..	80.0	93.3	..	88.9	93.3	..	82.3	91.0	..
(G) Soap	66.5	80.2	74.0	68.6	90.7	78.9	88.3	84.0	84.0	78.3	87.7	83.5

TABLE VI. AVERAGES OF FIVE WASHES FOR FOUR PIGMENTS (FROM TABLES I, II, AND V) SHOWING EFFECT OF DETERGENTS AND INTERFERENCE CAUSED BY CALCIUM CARBONATE PLUS CARBON DIOXIDE, AND CARBON DIOXIDE ALONE

	DISTILLED WATER		WATER + $CaCO_3$ + CO_2		WATER + CO_2	
	Av. reading	Gain due to detergent	Av. reading	Loss in efficiency due to $CaCO_3$ + CO_2	Av. reading	Loss in efficiency due to CO_2
REMOVAL OF PIGMENT						
Water, no detergent	43.9	..	36.2	7.7	38.8	5.1
Silicate alone	55.0	11.1	51.4	3.6	55.8	None
4 silicate, 1 soap	61.1	17.2	55.8	5.3	61.1	None
1 silicate, 1 soap	60.8	16.9	58.0	2.8	65.0	Gain
1 silicate, 4 soap	67.2	23.3	56.9	10.3	64.7	2.5
Soap alone	64.9	21.0	48.1	16.8	57.9	7.0
PROTECTION AGAINST REDEPOSITION						
Water, no detergent	60.9	..	50.1	10.8	53.0	7.9
Silicate alone	77.6	16.7	68.2	9.4	77.1	0.5
4 silicate, 1 soap	86.7	25.8	76.1	10.6	85.1	1.6
1 silicate, 1 soap	88.6	27.7	84.5	4.1	87.3	1.3
1 silicate, 4 soap	89.6	28.7	83.4	6.2	89.9	Gain
Soap alone	89.8	28.9	76.0	13.8	85.6	4.2

ing formation of sodium bicarbonate not only decreases the alkalinity, but probably the calcium soap sticks to both the clean and dirty cloth and holds some pigment. There is a distinct yellow tint on some of the cloth washed with soap. This is believed to be indicative of the presence of calcium soaps. It was much greater in the first series where the rinsing was done with hard water. Apparently the calcium soap stuck more readily to the clean than the soiled cloth.

CONCLUSIONS

1. The presence of calcium bicarbonate in water interfered seriously with the action of sodium oleate in removing pigments from cloth and in preventing their redeposition on clean cloth in the same solution.
2. The effect on mixtures of soap and sodium silicate (Na_2O:3.25SiO_2) or on the latter alone was much less.
3. Therefore, the mixtures become better than the soap both in removing pigments and in preventing their redeposition.
4. The effect is apparently partially due to the formation of acid soap and partially to precipitation of calcium compounds.
5. In the range studied, the detergent effect was not proportional to the pH.
6. Carbon dioxide has an appreciable effect in decreasing the removal of pigments by soap solution and increasing redeposition.
7. The addition of sodium silicate (Na_2O:3.25SiO_2) largely or entirely neutralizes the effects due to carbon dioxide.
8. A duplicate run gave close checks.

The effect of other water constituents will be discussed in later papers.

LITERATURE CITED

(1) Burkhart and Falkman, *Oil & Fat Ind.*, 8, 416 (1931).
(2) Carter, IND. ENG. CHEM., 23, 1389 (1931).
(3) Rhodes and Bascom, *Ibid.*, 23, 778 (1931).
(4) Snell, *Ibid.*, 24, 76 (1932).
(5) Vail, *Oil & Fat Ind.*, 8, 413 (1931).

RECEIVED September 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.

Research on Metals and Alloys

F. C. FRARY

Aluminum Company of America, New Kensington, Pa.

THERE are two fundamental objectives in research on metals and alloys. The first may be said to be academic or theoretical in its nature, and involves the investigation and the understanding of the complex physicochemical intermetallic systems and the effects of variations in temperature, minor impurities, and other variables upon such systems. The second objective, which we might call the practical or commercial one, comprises the improvement of our present alloys and metals, so as to make them more widely adaptable or more useful to mankind, and the discovery of any possible new and useful alloys. Experience shows that the second of these objectives cannot be pursued to the best advantage without a simultaneous pursuit of the first one. Conversely, it would be suspected that even those investigators whose viewpoint, experience, and interest lie only in the theoretical realm, would do better work in their chosen field if they had more information as to the practical facts and conditions which are involved and are important in the commercial production and use of metals and alloys.

Research on metals and alloys differs from most chemical research in that, in general, we are never dealing with pure compounds but with intimate mixtures of elements with certain more or less loose intermetallic compounds, and solid solutions of one in the other. Moreover, many of the changes involved take place at relatively high temperatures, and physical phenomena, such as melting, crystallization, precipitation in the solid state, recrystallization, crystal distortion by cold work, and many others complicate the problems from a practical point of view. Also, in the case of metals and alloys, the physical properties are generally the most important; the chemical properties are generally of minor interest except in so far as the problem of corrosion resistance is involved.

EFFECT OF IMPURITIES IN METALS

In the study of metals and alloys, increasing evidence is being found of the great effect which the presence or absence of small amounts of certain constituents may have on many of the properties of the resulting product. The segregation and crystallization of such minor constituents at temperatures above the freezing point of the molten alloy may cause troublesome drossing: if, on the other hand, they remain liquid at temperatures considerably below the freezing point, they tend to be concentrated in the grain boundaries of the crystals which form during the freezing, and this concentration may lead to a variety of effects, such as intergranular corrosion, hot-shortness, etc.

Some of these minor constituents may, by their behavior at the freezing point of the metal, interfere with the freezing and cause supercooling to a considerable extent. This is the case when about 0.01 per cent or less of sodium is present in certain aluminum-silicon alloys, where the molten sodium appears to be precipitated out at the freezing point and, by its action on the crystal nuclei of the silicon, to prevent the normal growth of these nuclei until the temperature has dropped about 10° or 15° C. below the point at which freezing should begin. Thereupon the crystallization force of the silicon becomes so great as to produce a perfect shower of nuclei, resulting in the crystallization of the silicon in almost submicroscopic crystals throughout the mass of the aluminum. Such a change also involves a considerable change in the strength and ductility of the resulting alloy and may be taken as a typical example of the pronounced effect which small traces of constituents may have in modifying the behavior of other constituents present in a relatively large amount.

The effect of traces of certain elements, such as arsenic, on the electrical conductivity of copper, the effect of slight variations of sulfur and phosphorus on the properties of iron and steel, and the effects of very small amounts of lead in brass, are all common illustrations of the importance of extremely minor amounts of certain constituents, and the complications which may be involved in alloy problems by lack of knowledge or control of the presence of some minor impurities. There are many less common examples of the same effect which need to be studied and may be of considerable importance.

Very often minor insoluble impurities may have a large effect upon the size of the crystals of the metal which forms the main body of the alloy. This effect may be exerted on the crystal formed in the original freezing of the alloy, where small amounts of solid constituents, if present, may act as crystal nuclei and thus facilitate crystallization from a multitude of centers and consequently produce a fine-grained structure in the castings (which is very much to be desired). Also, the same or other constituents in an extremely finely divided state may seriously interfere with or modify the effects of subsequent annealing and heat-treating processes. These minute insoluble particles in the solid metal seem to have a powerful restraining effect on the growth of new crystals, which is one of the important phenomena occurring during annealing. If present in the proper proportion, they may give rise to a very fine-grained and consequently very desirable structure, while a slightly different proportion may interfere in a different way with the crystal growth and result in the formation of fewer and larger crystals which are likely to be extremely objectionable if the metal is to be subsequently worked. The presence of 0.1 or 0.2 per cent of an impurity may raise the annealing temperature of a metal over 100° C. Electrical and thermal conductivity, corrosion resistance, and the brittleness or ductility of an alloy seem to be especially prone to be markedly affected by small amounts of minor constituents.

It is therefore obvious that a modern investigation of an alloy system demands as starting materials metals of the highest degree of purity, and it is this effect of minor impurities which renders inaccurate much of the older work on alloy systems. It is for this reason that investigators have spent years of time and vast sums of money in producing metals in a state of as nearly spectroscopic purity as possible.

WORKABILITY

One of the important properties of a metal or alloy is its workability. This is often a function of its crystalline structure, in which the author includes not only the system of crystallization as shown by x-ray analysis, but also the size of the crystal units making up the solid metal. Certain types of metal crystals (for example, those belonging to the hexagonal system) have inherently only a limited workability because of the arrangement of the atoms in the crystal. The frequent annealing required to overcome this difficulty adds considerably to the expense of working. Annealing consists essentially in heating the metal to such a temperature that its atoms become sufficiently free to move, so that they have a chance to rearrange themselves into new, undistorted, and unstrained crystal forms. Thus the internal effects of the prior cold-working are largely eliminated, and we may in a very real sense begin over again with our working operations.

For the best results, annealing conditions should be so chosen as to produce a finely crystalline rather than a coarsely crystalline structure. If the metal has sufficient strength and ductility to endure working at temperatures above the annealing point, much difficulty may be avoided by carrying on the operations at such temperatures. Then the rearrangement of the atoms after the working is substantially instantaneous, and consequently the speed of working can be much increased. Unfortunately, however, some of the alloying constituents, as have been indicated, by segregation in the grain boundaries or in other ways, tend to produce a condition of hot-shortness which locally weakens the metal at elevated temperatures, making it very difficult to work without cracking and consequently spoiling the metal for commercial use.

Cold-working, on the other hand (except in the case of metals such as tin, which anneal at or below room temperature), by causing motion of the atoms in the crystals along certain slip planes, produces a considerable strain-hardening or strengthening effect; so that the tensile, yield, and compressive strengths of the metal are increased, while its elongation or ability to stretch is decreased. Since this is often a desirable improvement in the properties of the metal, the ability to withstand cold-working is an important one. Here again, the presence of certain constituents and their segregation during the freezing of the molten metal may result in local weakening, so that the metal will crack under the working strains. Also, the increasing amounts of alloying ingredients required to give increased strength generally tend to reduce ductility and consequently make cold-working more difficult.

The problems in annealing and heat-treating metals are often quite involved. Aside from possible allotropic changes, as in the case of iron, we have the possibility that constituents which were insoluble in the original cast alloy may go into solution and change their distribution upon heating, and may come back out of solution in quite a different form and position upon cooling again. The rate of cooling is often decisive as to this latter possibility. Moreover, the rate of heating, especially the rate of passing through certain critical temperatures where the recrystallization or annealing process is just beginning, and the amount of cold work which has been accomplished on the metal before the annealing or heat treatment, often control the size of the grains produced. Also, cold-working lowers the recrystallization temperature more or less. A mistake in controlling one of these conditions may have quite disastrous results as far as the physical properties of the finished article are concerned. Consequently one of the aims of research in metals and alloys is to understand, as completely as may be, the theory of such crystal growth and its control, so that the practical man may know where to look for the causes of his trouble and how to avoid them.

PROBLEMS OF MELTING METALS

The problems of the melting room are both chemical and physical in their nature. Contamination by the chemical action of air, refractories, or any slag present, must always be considered and may be important, while the more or less mechanical inclusion of insoluble oxides, gas, etc., may cause serious defects in the finished articles. In some metals we have a real solubility of the oxide in the molten metal, and, as would be expected, even small amounts of such dissolved oxides have marked effects upon the properties of the metal. On the other hand, hydrogen seems to be soluble in many molten metals, and to be given off again on freezing, to form blowholes. The tendency of the metal to form dross by oxidation or by the precipitation of undissolved particles at the casting temperature is of great importance, not only from the standpoint of making clean castings, but also from that of making the metal run properly in the molds, and thus produce castings which are free from what the foundryman calls "cold shuts," or places where two semi-fluid streams of metal meet but fail to unite completely and fill the mold.

The questions involved in the behavior of the metal during solidification—i. e., the amount of shrinkage involved in freezing, and the temperature range within which freezing takes place, as well as the viscosity of the partially frozen or mushy metal—are of great importance in the casting of the metal. Since, in general, melting and casting are the first operations in producing any kind of a metallic body, it will be seen that these problems are fundamental.

In many cases we have special treatments producing a hardening or softening of the surface, such as the nitriding and malleabilizing processes used in the iron and steel industry.

These usually depend upon chemical reactions between certain constituents of the metal and certain constituents of its environment, both of which, of course, must be controlled. The fact that oxygen and nitrogen are often involved in such changes may decidedly complicate many of the heating operations necessary in the commercial working of metals, so that the importance of thoroughly understanding these changes is apparent.

Customers' Problems

There is also a great variety of what might be called "customers' problems," having to do with the utilization of the finished product. Thus the problem of machining certain alloys is difficult, and steps must be taken either to improve the material of the tools, change the alloy so as to make it more easily machinable, change the shape or speed of the tools, or otherwise alter the conditions so as to make the use of the alloy economical.

In many cases the customer is not so much interested in the properties of the article at ordinary temperatures as he is in its properties at relatively high temperatures. A good example of this is found in the heads for airplane engines where the important property is a high strength at temperatures of 300° to 450° F. (150° to 230° C.). Sometimes the physical properties at very low temperatures become important. Fatigue phenomena—formerly erroneously ascribed to "crystallization" of the metal under vibration—are sometimes very disturbing and very hard to understand. Their investigation is an important branch of the study of metals and alloys.

In the practical problems we always have to consider the commercial angle. The alloy must not only fulfill the technical requirements of the customer, but it must be salable; its cost in the form of the finished article must be reasonable and satisfactory to the customer. This requirement naturally includes not only the cost of the ingredients of the alloy but especially the costs involved in getting it into the desired form. These naturally depend upon the amenability of the alloy to various fabricating practices. In some cases we have a choice between a number of processes of producing the finished article; and there, of course, the intimate knowledge of the characteristics of the processes themselves and of the behavior of each alloy in such processes is of great importance.

Casting Processes

The casting processes are often the simplest means of producing a given article, and here we have to choose between sand-casting processes, which may employ either green sand molds or the more expensive baked sand molds, and various types of chill-casting processes. The chill-casting processes are so called because they involve the use of a metal mold which, because of its high thermal conductivity, rapidly chills and freezes the molten metal. This has a general tendency to produce a casting with finer grain and higher strength and elongation, but the chill molds are naturally expensive and therefore out of the question unless a large number of pieces are to be made from the same pattern. Moreover, the size of articles which can be made in such metal molds is strictly limited, except for such simple shapes as rectangular blocks or ingots which are used as a starting point for working processes. These are practically always cast in metal molds and the technic of producing them has gradually improved, so that extremely large ingots are cast in some cases.

Where an article is to be cast which has very thin walls, difficulty is often experienced because of the freezing of the alloy before the thin-walled portions are completely formed, causing what the foundryman calls "miss-runs." Obviously, there are two ways of avoiding this: the use of hotter molds or metal, or a more rapid introduction of the metal. The allowable metal and mold temperatures are usually limited, not only because of oxidation or other difficulties during the casting period, but also because higher temperatures usually give castings of coarser structure and lower physical properties. A rapid introduction of the metal, is, in general, feasible only if the metal can be introduced under pressure, and this is the basis of the so-called die-casting process by which millions of small thin-walled castings are made every year. The molten metal is usually forced into the die or metal mold by means of air pressure, which may be as high as several hundred pounds per square inch. The extremely rapid flow or squirting of the metal into the die naturally produces turbulence and the inclusion of a certain amount of air, so that these castings are likely to have air bubbles in them, but they can be made very accurately to size and can be provided with inserts of other metals and with cored-out holes in all directions, so that for a great many purposes they are practically ideal.

For each of these casting processes we have certain alloy requirements, and one of the important commercial problems in the casting industry is the adjustment of the physical and chemical properties of an alloy so as to meet the customer's requirements along these lines, and at the same time to permit the casting to be made by the process which will give the most economical results from the customer's viewpoint.

The different methods of working metals and alloys each has its own peculiar effects and characteristic limitations. Hammer-forging was probably one of the earliest methods of working metal and is still used for many purposes. Here we have to deal with deformation under impact—heavy local compressive stresses suddenly applied to the hot metal. Because of the possibility of turning the article and applying these stresses in two directions at right angles to one another, or even in a variety of directions in the same plane, this method of working may be somewhat easier on the metal than rolling. The possibility of combining a rough shaping operation under the hammer with a finishing operation involving the hammering of the rough piece between two parts of the die, thus producing a worked article of irregular shape and thickness, makes this process particularly applicable to certain types of articles, such as connecting rods. Some metals and alloys, however, do not withstand the sudden application of such forces to the hot metal nearly as well as they do a more gradual application of pressure, so that the forging operation may in some cases be advantageously turned into a pressing or squeezing one.

A logical modification of the pressing or squeezing operation is the process of extrusion, where heavy pressure is applied to an ingot in a confined space, and the hot plastic metal is forced through a die so as to produce a long member of uniform cross section, such as a rod, a piece of pipe or molding, etc. Here we obtain a thorough working of the metal, but we have decided limitations because of the varying degrees of plasticity of different alloys at the allowable working temperatures, the surface-tearing effects of friction between the moving metal and the dies, and the high-pressure and consequent heavy and expensive construction of the press required for handling strong metals and alloys. In some extruded articles the final shape and finish are of chief importance, and soft, readily worked material may be used. In others we have requirements of color, corrosion resistance, machinability, flexibility, etc., and in some cases high mechanical strength and ductility are necessary. Here again, the choice of the alloy and the adaptation of its composition to the requirements of the working process, as well as to the requirements of the customer, are of importance, and involve the accumulation and correlation of a great deal of detailed information.

Many metals and alloys are produced and used in the form of rolled sheet of varying gages, from foil a few ten-thousandths of an inch in thickness up to slabs or plates which may be several inches thick. Here again, we have a highly localized stress applied progressively across the surface of the ingot or slab as it passes through the rolls, producing severe compression stresses and also severe tension stresses in the metal as it is forced forward through the rolls. However, in this case the force can be applied only in one direction and may have a decided tendency to tear the edges of the sheet and produce cracks extending inwardly from the edge, which may cause the loss of a good deal of the product. In general, therefore, rolling is much harder on the metal than either forging or extrusion, and an alloy which is to be worked by rolling must be more workable at high temperatures than one which is to be forged or extruded. The rolled sheet after annealing may have to be drawn in dies or spun, and here other qualities of plastic flow at ordinary temperature become of great importance. In some cases the metal is required in the form of wire or rod, which allows us to use a rolling process that is easier on the metal than the sheet-rolling process. This is followed by drawing through dies where the metal is elongated by stresses, both in tension and compression. In studying a new alloy, its behavior under all these different fabricating processes has to be determined experimentally before it can be offered to customers.

In the customer's plant the metal may have to undergo many auxiliary fabricating operations such as shearing, punching, bending, straightening or flattening, welding, riveting or soldering; each has its own peculiar set of difficulties and involves localized mechanical or thermal stresses, the effects of which must be thoroughly known. The working out of the proper technic for such operations, as each must be modified by the varying properties of alloys and varying mechanical conditions in the articles to be fabricated, is of itself no small problem.

CORROSION PROBLEMS

One of the major problems of the metal industry for many years has been that of corrosion. Of course the manufacturer does not wish his product to last indefinitely, but the customer is likely to have such a desire, and the manufacturer must try to meet the demand. Studies of the cause and mechanism of corrosion are of great importance but not always as simple as they appear to be, because often the influence of a variety of manufacturing factors have to be considered which may be quite unknown and out of the control of the independent investigator. Changes or variations in methods of working, thermal treatment, slight variations in composition, variations in soundness or in crystal size, may all decidedly influence the results. For this reason, such investigations, like most of the investigations already mentioned, require as their background a detailed knowledge of the metal-working industry, and particularly of the methods of fabrication of the articles being studied, and a considerable amount of control over such fabrication.

We have also the problem of protecting metal articles from corrosion by various surface coatings and other treatments, and the investigation of the specific effects of different corrosive media on different alloys. A branch of this problem which is of interest to chemists is the fact that even relatively slight corrosion of certain metals or alloys used as containers in some chemical or food industries, by putting traces of certain metals into solutions in the product, may have profound effects upon the reactions taking place in the container, particularly if these reactions involve bacteriological changes or the growth of molds or similar low forms of life, or if the product is affected by the presence or absence of sensitive substances such as vitamins. Some puzzling differences in the behavior of apparently identical pieces of equipment in such processes have been shown to be due to the presence of small amounts of certain elements in the one case and their absence in the other. Even a slight corrosive effect of the vessel contents may be sufficient to dissolve enough of the metal—in some cases only of a fraction of a part per million of the solution—to account for the differences.

When we consider the great changes in temperature involved in the fabrication of metal articles, it is not surprising that residual stresses should be encountered in the finished article. Some of these stresses are of a mechanical nature and some might be said to be of a chemical nature; that is, the article in question may be physically strained on account of sudden temperature changes to which it has been subjected or because of work which has been done upon it, or it may be constitutionally somewhat unstable because the constituents are not in equilibrium at room temperature, although they may have been in equilibrium at the higher temperature at which the article was formed. Thus in some alloys we have to consider the problem of stability on aging or machining; sometimes the removal of a very light cut from the surface of a beautifully flat slab will cause it to curl and twist because of the presence of internal stresses, some of which have been unbalanced by the removal of the surface layer. In other cases the article may gradually change its dimensions, usually in the direction of a slight increase in size, upon long standing—that is, after it has been machined and put into service. This is particularly likely to occur in some alloys if the article is repeatedly or continuously heated to moderate temperatures. The prevention of such phenomena of growth and the removal of internal stress are problems which have taxed the ingenuity of investigators in the alloy field.

Simple as the metallic systems are in their constitution and their formulas as compared with the materials of organic chemistry, or even the more complicated of the fields of inorganic chemistry, it is hoped that this review has shown enough of the complexity of the problems of alloy investigation so that it will be clear that there is something involved in the production of a new commercial alloy beyond the mixing of a few metals in proportions not hitherto published, and the obtaining of a patent upon such a composition. It will also be clear why in this line, as in most other well-developed practical lines of research, investigation by persons not highly skilled in the art and not in close touch with actual manufacturing conditions is extremely unlikely to produce results of any real value, and why industries themselves must maintain large staffs of men with a variety of types of training and fields of work in order to make progress in the development of new and useful processes and products in the metal industry.

RECEIVED September 27, 1933. Presented before the General Meeting at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.

NEW GERMAN ZINC PLANT TO COMMENCE OPERATIONS NEXT SUMMER. The new German zinc works which is being constructed at Magdeburg is expected to be ready for operation in July or August, according to information made public by the Commerce Department.

The plant will have an annual capacity of 40,000 metric tons of refined zinc, but provisions are being made so that the plant can be enlarged to produce 60,000 tons per year, if required. At the present time, Germany imports approximately 100,000 metric tons of zinc each year.

It is estimated that the plant under construction will cost about 18,000,000 reichsmarks, the project being largely financed by the government with funds available for decreasing unemployment. The electrolytic principle will be employed to produce refined zinc from zinc ore originating chiefly in German Upper Silesia.

The Sorption of Water by Cellulose

S. E. Sheppard and P. T. Newsome, Eastman Kodak Research Laboratories, Rochester, N. Y.

The sorption of water by cellulose is one index of the fine structure of the gel. The sorption of water vapor is determined by two phases or stadia, continuous with each other. There is a primary surface or chemosorption, dependent on the free hydroxyls. Water molecules are held to these by strong forces, considerably greater than for the condensation of water vapor. There is also a volume sorption, or capillary condensation.

Mercerization—i. e., treatment with caustic alkali solutions of 18 per cent or higher, followed by washing out the alkali—gives a cellulose with a coarser lattice structure and higher water absorption at all vapor pressures. Similar materials are obtained by "regeneration" of cellulose from cuprammonium solution or from viscose, as also by hydrolysis of cellulose esters reprecipitated from acetone solution. These are termed "hydrate celluloses." On the other hand, degrading treatments, such as acid tendering and oxidation, do not materially change the water adsorption.

Wood pulp (alpha-pulp) has a higher sorption than cotton cellulose, approaching mercerized cellulose. But the sorption of water vapor is unaffected by beating ("hydration").

"Hydration" comprises effects depending upon increase of external surface or dispersity. This increase permits closer interlocking of the dried felt or sheet, hence, inter alia, lower absorption, and retention of liquid water thereby.

The relation of cellulose to water was regarded by those great pioneer cellulose chemists, Cross and Bevan, as a critical characteristic. It is true that they appear at one time (*4*) to have considered the water retained as forming a continuous series of hydrates, a view which subsequent investigation has abandoned. But that is a question of terminology. The persistence of such terms as "hydrate cellulose" and "the hydration of cellulose" illustrates this. But in their emphasis on the importance of cellulose hydroxyl groups for water attraction and on the continuity of the phenomena for different forms and derivatives of cellulose, they divined the fundamentals.

We may distinguish between two main regions of interest—viz., cellulose (and cellulose products) in the presence of water vapor and again in the presence of liquid water. The practical importance of humidity for the behavior of cellulose materials needs no amplification, no more than does the relation of liquid water (including aqueous solutions) in the mechanical handling of cellulose pulps, the wet strength of cellulose products, and the like. The contribution to be made here is a brief account of some investigations whose primary objective was the less hygroscopic cellulose derivatives (esters, etc.) which required consideration of the more hygroscopic celluloses themselves.

Cellulose Nomenclature

Because of the multifarious variety of cellulose materials, it is desirable in any account of experimental observations to specify as explicitly as possible the origin and previous treatment of the cellulose specimen in question. Raw cotton comprises both long staple and linters, but linters will generally have received chemical treatment (kiering, bleaching) before being further examined. Again, the terms "oxycellulose, hydrocellulose, alpha-cellullose," etc., require explicit definition if and whenever used.

Sorption Analysis of Cellulose

The study of the sorption of water, as of other molecules, by cellulose materials, comprises three main devisions:

(1) Statics of sorption—i. e., adsorption and desorption isotherms. Such isotherms usually refer to the relations of moisture regain or retention to vapor pressure. But other isotherms are of interest here in imaging the relation of water molecules to the cellulose. Such are isotherms of electrical resistance (or conductance) as function of water content, and of mechanical rigidity. (2) Kinetics of sorption—i. e., velocities of sorption and transpiration of water or other vapors and liquids. (3) Energetics of sorption—e. g., heats of sorption and wetting.

Vapor Pressure Isotherms

Measurements of moisture regain and loss at different vapor pressures have been made by many observers on a wide variety of cellulose bodies. In this laboratory the convenient McBain-Bakr adsorption balance has been largely though not restrictedly employed, and its use for this purpose is extending. According to the purpose and requirements, the vapor pressure may be: (1) stationary final value of limited volume of vapor in contact with cellulose sample, (2) equilibrium value of pressure of large ballasted volume of vapor, (3) dynamic equilibrium value of current of vapor. For most purposes under discussion these values are equivalent.

Typical isotherms at 30° C. obtained in this laboratory are shown in Figure 1. The standard cellulose was prepared according to the method of Corey and Gray (*3*) from good grade cotton. The linters were a good grade, merely alkalikiered, and slightly bleached.

The term "hydrated cellulose" in this paper is applied, in contrast with "native cellulose," to those forms of cellulose which show the x-ray diagram characteristic of soda cellulose after washing out the alkali (mercerized cellulose). The differentiation between the diagrams of native and mercerized cellulose is dealt with elsewhere (*26*). Essentially it appears that the most important characteristics of hydrate cellulose in comparison with native cellulose are accounted for by assuming that the hexose units of the primary valence chains are so rotated with respect to each other that their planes become approximately perpendicular. As the basis (elemental) cells are at the same time somewhat separated in both directions, mercerization involves a slight pushing apart of the axially parallel cellobiose chains.

Compared with the configuration of the lattice of native cellulose, that of hydrate cellulose is a less strained one, lower in energy, and more stable. It is not surprising therefore that after operations such as (1) dissolution of cellulose in cuprammonium and regeneration, (2) dissolution of soda cellulose in carbon disulfide (xanthogenation, viscose) and regeneration, (3) esterification, solution, regeneration, in all cases the regenerated celluloses show the hydrate cellulose diagram. It is probable, however, that concomitant with the distention of the lattice structure there occur greater or less secondary swellings, increasing the total surface. Thus the regenerated celluloses appear to have a somewhat more open structure than the directly mercerized cellulose and, as simple celluloses, show the highest water adsorption which has been observed in this laboratory.

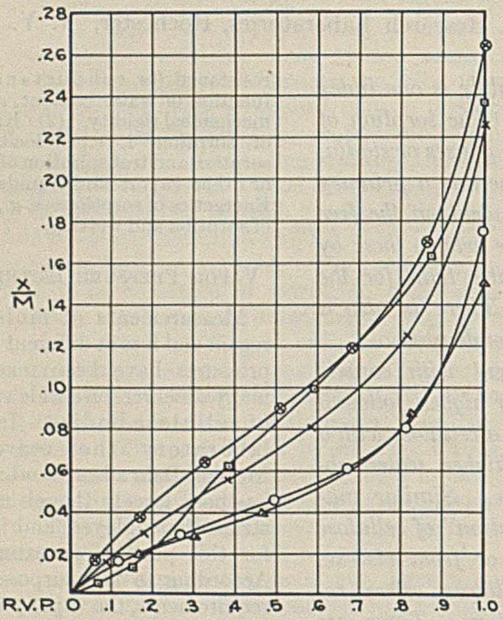


FIGURE 1. ABSORPTION OF MOISTURE AT 30° C. BY:

○ Standard cellulose × Hydrate cellulose A
△ Cotton linters □ Hydrate cellulose B
⊗ Hydrate cellulose C

COTTON AND WOOD CELLULOSE

In comparing cellulose specimens of different origin in respect of a property such as sorption, it is evident that certain criteria of purification and treatment must be adopted which should bring them to a common level for the chemical species, cellulose. For, obviously, different raw materials may contain impurities (noncellulose materials) either hygroscopic, or, like waxes and resins, decreasing water sorption. The comparative data now presented cannot be regarded as strictly complying with these criteria. Again it can be demonstrated (and, as discussed later under "Hysteresis," it is indeed an inherent characteristic of cellulose bodies) that the previous history of the specimen in regard to uptake (regain) and loss of water significantly affects its apparent equilibrium value under a specified condition. It is desirable, therefore, that investigators should agree not only on certain standard states but on the path by which the specimens are brought to these. Comparison of sorptions for specimens (1) dried at 100° to 105° C., then moistened; (2) dried by evacuation at x mm.; (3) dried over P_2O_5 then humidified at x per cent relative humidity will show minor but not very important differences *inter se*. But comparison of any one brought to equilibrium vapor at 90 per cent relative humidity, then dehumidified at x per cent relative humidity, will show very large differences.

The data for comparing cotton cellulose and wood cellulose are still rather deficient in all of the forenamed aspects. But it is worth presenting them, if only to obtain a better comparison later. The writers have compared their own values for cotton cellulose with data from the invaluable work of Urquhart and Williams (*33*), and with these, data on cotton cellulose, wood, and pulp from Pidgeon and Maass (*21*). The data of Oguri (*19*) are noted also in this connection.

TABLE I. COMPARATIVE MOISTURE ADSORPTION OF COTTON AND WOOD CELLULOSES AT 23° C.

Vp	COTTON (*33*)	COTTON (*26*)	COTTON (*21*)	SPRUCE WOOD (*21*)	SPRUCE EXTRACTED (*21*)	α-PULP (SHEPPARD AND NEWSOME)
	%	%	%	%	%	
0.05	1.44	1.04	1.25	2.01	2.57	...
0.10	2.04	1.71	1.9	1.90	3.66	...
0.15	2.44	2.16	2.32	3.68	4.48	...
0.20	2.84	2.58	2.64	4.40	5.18	...
0.25	3.34	2.98	2.96	5.08	5.86	3.5
0.30	3.74	3.36	3.28	5.74	6.52	...
0.35	4.18	3.74	3.60	6.40	7.20	...
0.40	4.58	4.08	3.94	7.00	7.89	...
0.45	5.14	4.44	4.24	7.61	8.58	...
0.50	5.44	4.81	4.60	8.22	9.30	6.0
0.55	5.88	5.26	4.96	8.85	10.02	...
0.60	6.38	5.69	5.33	9.49	10.78	...
0.65	6.88	6.07	5.75	10.15	11.55	...
0.70	7.58	6.65	6.20	10.90	12.33	...
0.75	8.38	7.30	6.65	11.73	13.12	9.3
0.80	9.38	8.15	7.16	12.67	14.08	...
0.85	10.72	9.57	7.70	13.77	15.35	...
0.90	12.56	11.54	8.40	15.27	17.10	...
0.95	15.3	14.38	9.28	17.60	19.80	...
0.98	...	17.51	9.90	20.65	23.0	24.8

The values of moisture adsorption in Tables I, II, and III refer to moisture regain, at the vapor pressures specified, of dry materials (evacuated and dried at 105° C.).

The values obtained by the authors for standard cellulose are slightly lower than those of Urquhart and Williams for their "soda boiled" cotton. This might well happen if their "soda boil" was a somewhat more drastic alkaline treatment than that of the authors. A slight tendency to soda cellulose formation, or mercerization, would give the difference. On the other hand, Pidgeon and Maass' cotton values, while in reasonable agreement up to 50 per cent relative humidity, become surprisingly lower as the vapor pressure increases to saturation. Their values for extracted spruce wood do not disagree greatly with the few observations made by the writers on a high-grade alpha-pulp, which the latter do not wish to stress until extended. Their conclusion, that "cotton cellulose is fundamentally different from the cellulose in wood" (this is brought out by the adsorption curves not coinciding over any portion of their length) does not appear to be completely founded as yet. Grace and Maass (*7*), from later experiments exhibiting desorption curves, are somewhat more guarded. "The experiments of Pidgeon and Maass have been corroborated as far as these showed that the sorption of water vapor by wood is on a much greater scale than the sorption by cotton. This is true over the whole range of vapor pressures, both for the wood in its natural state and for extracted samples." It appears fairly certain from existing data that the sorption by wood and wood pulp is generally higher than that of purified native cellulose, approaching more that of "hydrate cellulose," and a careful examination

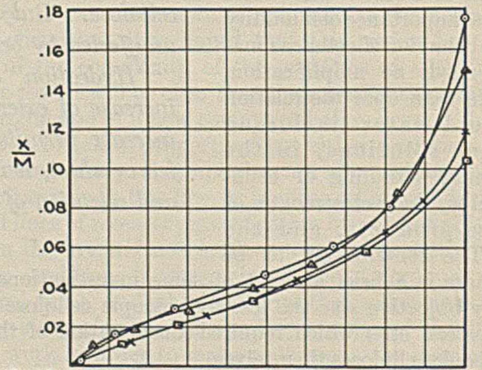


FIGURE 2. ABSORPTION OF MOISTURE AT 30° C. BY:

⊙ Standard cellulose × Oxycellulose
△ Cotton linters □ Hydrocellulose

of the x-ray diagrams is desirable.[1] However, treatments of cotton cellulose which do not give more than traces of change of x-ray diagram (peptization by calcium thiocyanate solution, and reprecipitation) can also considerably raise the whole moisture regain, but more especially at higher vapor pressures.

Urquhart and Williams, and Newsome and Sheppard both dried their cotton cellulose at 105° C., whereas Pidgeon and Maass apparently took as dry weight material evacuated over P_2O_5.

Oguri (*19*) by comparison of cotton with bamboo pulp celluloses, concluded that "bamboo cellulose—i. e., the Keichikn cellulose and the bamboo pulp—are more hygroscopic than the native cotton cellulose and resemble the mercerized cellulose." To summarize, the evidence available indicates that wood cellulose has a looser gel structure, greater inner dispersity, than native cotton cellulose.

Degradation of Cellulose

Treatment with oxidizing agents under specified conditions (*26*) gives materials variously termed "oxycelluloses," or "oxidized celluloses," of which the latter is preferable. Undoubtedly part of the effect consists in a degradation, a shortening of the macromolecules or chains, which is the principal difference effected in so-called "hydrocellulose." This is a term sometimes applied to cellulose treated with solutions of mineral acids whereby a greater reactivity to esterifying agents is obtained as well as a higher copper reducing number, greater extraction value by 17.5 per cent caustic alkali, and lower viscosity in cuprammonium solution. These partially degraded celluloses, when thoroughly washed and dried, sometimes show a lower moisture adsorption than the original from which they are prepared (Table II, Figure 2).

Table II. Moisture Adsorption of Degraded Cellulose

Material	Viscosity	Moisture Regain at 100% Relative Humidity (30° C.)
	Centipoises	%
Standard cellulose	400,000	17.5
Linters	4,800	15.0
Hydrocellulose	10	10.4

On the other hand, there is no evidence available that the molecular weight of the cellulose, in so far as indicated by viscosity measurements, shows any correlation with water adsorption. The data of Table III on different samples of cotton linters show this.

Table III. Moisture Adsorption of Cotton Linters

Sample	Viscosity	Regain at 25° C. 50% relative humidity	Regain at 25° C. 100% relative humidity
	Centipoises	%	%
b-16-596	75	5.4	17.1
c-16-596	215	5.4	17.3
e-16-596	360	5.3	17.1
d-16-596	1038	5.4	17.4
f-16-596	1650	5.4	17.2
g-16-596	5770	5.4	17.9
h-16-596	7400	5.6	17.7

The same thing was found for regenerated celluloses of different viscosities. Furthermore, regenerated celluloses of quite low viscosities (10 to 15 centipoises) showed sorption values much greater than those of native celluloses of much higher viscosities (2000 to 40,000 centipoises).

The conclusion from this is that the "fine structure," or arrangement of atom groups in a lattice, as well as the nature of certain of these groups, is of much greater importance for the water sorption of cellulose complexes than the magnitude of the chain molecule. This is borne out by the behavior of derivatives, such as esters and ethers, as contributing indirect evidence on the case of cellulose. The essential facts are (*26*):

(1) With degree of esterification, up to the triester, water sorption is progressively reduced.

(2) Esters produced by solution (dope-esterified) or reprecipitated from solution, show higher water sorptions than undissolved fibrous esters of the same composition. These esters show transition to the hydrate cellulose lattice.

(3) Other things being equal, the water sorption is reduced with increase of molecular weight of the esterifying or etherizing group (*24*).

From these results two conclusions can be drawn with regard to water sorption by cellulose: First, the fundamental part is played by hydroxyl groups, which are removed by esterification or etherization. Secondly, however, since complete esterification with groups of low molecular weight still leaves a considerable value to the sorption, while esterification with groups of higher molecular weight reduces this to a very small value, there must be a residual sorption independent of the presence of free hydroxyls; this, however, is removed by increasing the weight of alkyl group combined.

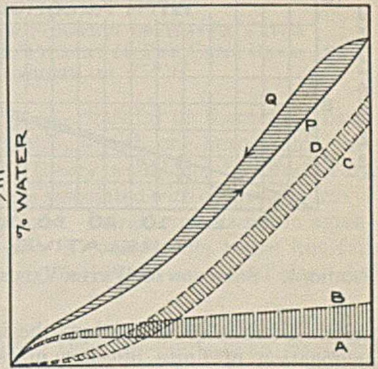


Figure 3. Ideal Sorption Isotherms

A. Initial surface saturation level
B. Actual surface saturation line
C. Initial capillary condensation
D. Actual capillary condensation
P. Observed adsorption isotherm
Q. Observed desorption isotherm

To explain these and other facts to be noted, the theory has been proposed that water sorption by cellulose materials depends upon two stages or phases. One of these, chiefly effective at low vapor pressures, consists in a surface adsorption of water molecules to free hydroxyl groups. On the one hand, it is evident that not every hydroxyl group is free in this sense, because, if it were, from the number of hydroxyl groups per hexose (C_6) unit, the water sorption would be many times greater than it is. On the other hand, it appears also that the surface in question cannot be the apparent external surface, because in that case the sorption would be much less than the actual value. Hence it appears that we must admit a certain porosity for water molecules and an inner surface. This is further consistent with the water sorption both of cellulose at higher vapor pressures and of cellulose triesters. The inner surface bounds the totality of inner pores or capillaries, in which fine gel structure water vapor is condensed (Figure 3).

The direct sorption of water is not followed by any significant change in the x-ray diagram, even though considerable swelling or increase of volume is attained. From this it is concluded that water molecules do not penetrate the elementary space lattice but only interspaces between definitely oriented regions. Katz (*8*) has distinguished this as intermicellar from intramicellar swelling. The micellar theory of cellulose structures (*12*) assumes that the fibers and other bodies are built up of ultramicroscopic crystallites, in which the atom groups are held in the space lattice, and that these crystallites are held together by looser secondary attractions. The attraction between the crystallites is all the stronger, the

---

[1] Since this paper was presented, a study of the x-ray spacings of wood cellulose has been made by S. Oguri [*Cellulose Ind.*, 9, 7 (1933)]. He finds that the actual intervals are identical with those of native cellulose from cotton.

better the orientation of these is in the sense of the primary space-lattice structure itself.

According to this conception, the primary adsorption is on the inner micellar surface, the capillary condensation in the intramicellar spaces.

While this hypothesis has proved to be and is still useful, the picture of the fine structure of cellulose materials (fibers, etc.) to which a number of investigators appear inclined is somewhat different in that it gives much less definite significance to the micelles as self-consistent and persistent units. Contrasted with a hypothesis of more or less regular aggregation of finite micellar units (which we may term "micellar aggregation"), it presents one of variable, partial, or regional molecular orientation, with no explicit units other than the fundamental atom groups—e. g., hexose units, and the primary valence chains, or macromolecules of these. The cellulose body or fiber then comprises regions of greater density of regular space-lattice orientation of these molecular and macromolecular units interspersed through, but continuous with regions of lesser degree of orientation and regular ordering. Linkage or bonding between adjacent atoms or groups varies from primary valence to electrostatic polarizations (dipole orientations).

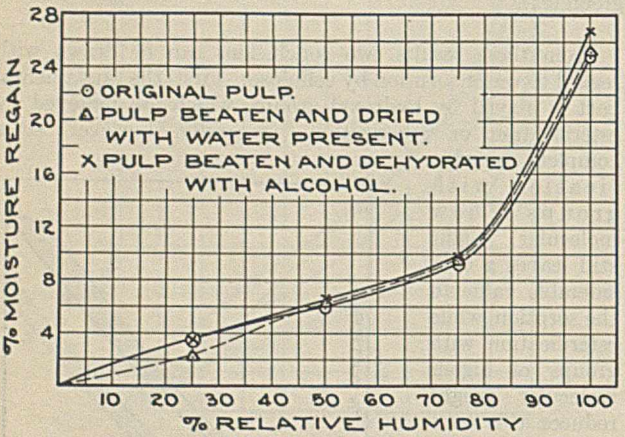


FIGURE 4. SORPTION OF WATER VAPOR BY WOOD PULP AT 25° C.

Evidence against persistence (or existence) of primary micelles, other than chain macromolecules, in solutions of cellulose esters is given in papers by Sheppard and collaborators (*25*). This has been confirmed and extended by other workers—e. g., by Trogus and Hess (*31*) from x-ray studies of swelling, by Katz and Samwel (*9*) from spreading of thin films. Again, arguments against assuming the rigorous micellar structure in cellulose fibers as conditioning nitration have been presented by Miles and Craik (*15*) and by Miles (*14*). Similar evidence, both from nitration and solution has been brought forward by Mathieu (*11*). The x-ray studies of Trillat (*30*) lead him to a conception of organogels forming from solution to give, as by an arrest of motion of molecular units, a more crystalline part interspersed through a less crystalline or amorphous part. The repudiation of the micellar hypothesis is most strongly voiced in recent papers by Neale (*16*) on cotton fibers, and by Astbury (*1*) for animal hairs (protein fibers). Neale's results—(1) that degradation by acids or oxidizing agents (hydro- and oxycellulose formation) while greatly reducing cuprammonium viscosity and tensile strength only slightly reduces moisture regain, (2) that mercerization little affects viscosity but greatly increases moisture regain (Neale's ratio at 50 per cent relative humidity 1.50, Sheppard and Newsome 1.51), (3) that regeneration, accompanied by degradation, decreases viscosity but greatly increases moisture regain (Neale's ratio 1.8 to 2.0, Sheppard and Newsome 1.9 to 2.0), are in good accord with those of the writers.

The data for the sorption of water are at present consistent with either hypothesis. For those who consider, with William of Occam, that *entia non sunt multiplicanda praeter necessitatem*, the micelle, so far as concerns cellulose and proteins, will be cheerfully consigned to oblivion.

SWELLING AND HYSTERESIS

Some decision (at any rate, further evidence) on this is furnished by the facts of swelling and hysteresis in the sorption of water by cellulose. As stated, the sorption is not accompanied by changes of the x-ray diagram. This requires, therefore, a distention which does not affect the well-oriented regions. The cause of swelling has been much discussed (*8*). The hypothesis of osmotic pressure by solution of a more soluble portion within an insoluble portion proposed by Northrop and Kunitz (*18*) for gelatin hardly appears applicable to well-washed and extracted cellulose materials. It appears more probable that we are dealing with a relief of local strains, consequent on the uncoupling of polarized hydroxyl groups. These are, however, relatively isolated and singular groups in less oriented, amorphous regions; otherwise changes of x-ray dimensions would be indicated.

The swelling, as change of total volume, is not completely reversible, and neither is the sorption of water. The desorption isotherm lies above the adsorption one. Repetition of the cycle reduces the hysteresis area but does not completely remove it.

The existence of limited swelling with the nonrigid or elastic gels requires clearer explanation than it has yet received. As against the osmotic theory (certainly applicable in certain cases, where a Donnan equilibrium can be verified) the alternative, or complement, appears to lie in the change of locally coupled chain-molecule configurations consequent on primary adsorption of water or other polar molecules. This type of action may pass over more or less continuously into so-called intramicellar swelling, and ultimately solution as the term of unlimited swelling. This theory is substantially an amplification of Urquhart's explanation (*32*) of hysteresis in terms of imperfectly reversible uncoupling of hydroxyl polarizations. One consequence of this is that in these elastic gels the gel fine structure, inner surface, and porosity previously mentioned are not relatively constant, as with rigid gels, but increase with the sorption. This will be discussed further with reference to the absorption of liquid water.

SORPTION AND SPECIFIC VOLUME

At various times investigators have suggested that adsorbed molecules, such as water in cellulose, are effectively under enormous compressive forces and have much lower specific volume (*8*). But the argument here, based on difference of apparent densities, neglects the question of the true volume of the swelling solid. Davidson (*5*) has pointed out that, if the density of cellulose is determined in helium, the value obtained should, assuming no "compressive adsorption" of helium, give the true specific volume. He obtained for cellulose, at 20° C., values around 0.64 for helium and 0.62 in water, from which he computes a contraction of the specific volume of adsorbed water from 1.00 to 0.93, or a compressive force of around 2000 kg. per sq. cm. However, the specific volume found in such diverse liquids as acetone, chloroform, etc., was also of the same order (0.64) as in helium. It seems reasonable that, if the wetting of a solid of high specific surface is small, the probable error on specific volume will be correspondingly larger. The case of helium is similar, since repulsion forces will be operative. The so-called compression of water here seems to be actually composed of the probable error of apparent density of the solid determined in a nonwetting or incompletely penetrating medium. The writers' values for cellulose in water and organic liquids agree with Davidson's, but they do not consider that his conclusion is binding. Data on the densities of a series of cellulose esters (acetates) point to the same conclusion. In water the density is a linear function of the acetyl content, whereas one would expect the compressively adsorbed water content to be changing and disturbing such a linear relation. The latter follows for additive molar volumes.

Inner and Specific Surfaces and Pore Volumes

Evidently the question of true specific volume defines both the void or pore volume, and the total (inner plus external) surface (or specific surface per unit mass). Actually these values have no purely geometric significance. They are measures of penetrability by molecules of given size and character. Thus we have found, from comparison of the heats of sorption of a series of alcohols with the magnitudes of adsorption, that alcohol molecules above *N*-propyl do not penetrate cellulose acetate. [The same limit was found by Speakman for wool fibers (*28*). This would indicate pore spaces of width not much greater than 7 Å.] From these data, inner or total surface values could be calculated, assuming monomolecular adsorption (*27*). Stamm (*29*), assuming compressive forces of the same order as Davidson, has calculated a "total surface" for wood of 0.3×10^6 sq. cm. per gram. Kalberer and Schuster (compare citation *13*) from assumed monomolecular adsorption of sulfur dioxide on native cotton cellulose, obtained 10×10^6 sq. cm. per gram. The writers' values for "diacetates" of cellulose are 6×10^6 sq. cm. per gram from direct adsorption limits (*27*) and from heat of wetting and adhesion tension 2.4×10^6. Assuming (for cellulose bodies) adsorption only to hydroxyl groups, this would give 18×10^6 sq. cm. per gram and 7.2×10^6 for cellulose. These values are nearer to Kalberer and Schuster's than to Stamm's.

Heats of Adsorption

Measurements of the heats of adsorption of water vapor to cellulose have been made by Urquhart and Williams (*33*) and by Oguri (*19*). The values of the former, calculated by application of the Clapeyron-Clausius equation to the change of adsorption with temperature, show a steady descent, for increment of water added, from 900 to 550 calories, the latter being substantially equal to the heat of condensation of water. Oguri's results differ considerably, in that he claims to find the initial heat of adsorption also equal to the heat of condensation, and a slight rise only up to about 6 per cent adsorption. The writers have measured the heat of adsorption of water vapor by a cellulose acetate (*17*) of 38 per cent acetyl (approximately diacetate). This was done both directly by calorimetric measurement and by calculation from the isotherms. In both cases *Q*, the differential heat of adsorption, fell with amount of adsorbed water, ultimately approaching also the heat of condensation. These results are in good agreement with those of Urquhart and Williams for cellulose itself. They confirm the view that the first adsorption of water—as that operative at low vapor pressures—involves a binding or chemosorption of different character from the later, larger amounts which are held by capillary condensation.

Mathematical Statement of Two-Phase Theory of Adsorption of Water

The two-phase theory of adsorption has been treated mathematically very ably by Peirce (*20*). Peirce's premises are "there are two distinct ways or phases in which water molecules are held in the cellulose—the (a) phase in which one water molecule is definitely associated with one hexose (C_6) unit as in a chemical compound, and the (b) phase in which the water molecules fill the spaces available under attractive forces like those in a liquid."

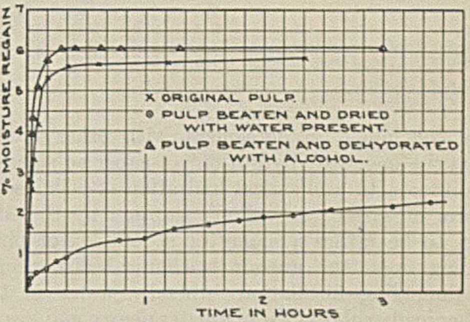


Figure 5. Rate of Sorption of Water Vapor by Sheets of Wood Pulp at 50 Per Cent Relative Humidity at 25° C.

There appears to be no experimental or theoretical basis for assuming one water molecule with one hexose unit, but actually the mathematical theory would not be affected by assuming one water molecule associated with one free hydroxyl —or indeed other assumptions. Peirce's results are in agreement with experiments over a considerable range but fail at the highest humidities (90 to 100 per cent) and also take no account of hysteresis.

Sorption of Liquid Water and von Schroeder Effects

The writers' results on the sorption of water by alpha-pulps slightly beaten (free pulp) and long beaten (considerably hydrated) agree entirely with those of Stamm (*23*) in the conclusion that the sorption of water vapor was unaffected (Table IV).

Table IV. Sorption of Water by Paper Pulps[a] at 25° C.

Material	50% Relative Humidity	100% Relative Humidity	Liquid Water
	%	%	%
Free pulp from paper mill	6.5	21.8	113
Slow pulp from paper mill	6.8	21.7	106
Slow pulp, ball-milled 4 hours, dehydrated with alcohol	...	24.3	...
Slow pulp, ball-milled 4 hours, dried with water present[b]	...	18.5	50
Slow pulp, ball-milled 48 hours, dehydrated with alcohol	...	24.1	...

[a] The pulp was a slightly bleached, highly purified sulfite pulp (alpha-pulp).

[b] Gave hard, horny translucent sheet.

One hundred per cent relative humidity refers to equilibrium values obtained after 24 hours on specimens in large desiccators over liquid water, the desiccators being kept in a thermostat at 25° ± 0.1° C.

The vapor adsorption isotherm of the slow beaten, strongly "hydrated" pulp sheet was substantially the same as that for the unbeaten pulp, with the following difference: If the sheet was dehydrated with alcohol prior to drying, a very slightly increased sorption at all vapor pressures was observed. If, however, the "hydrated" sheet was dried directly out of water, the apparent sorptions at low vapor pressures were definitely lower than for the free pulp sheet (Table V and Figure 4).

The deviation of the directly dried "hydrated" sheet appears to be larger because of a great slowing down of the sorption process. This is brought out in Figure 5. This horny sheet also showed evidence of discontinuities in the sorption process, as well as in the isotherm. These discontinuities may well be produced by a swelling process producing new adsorbing areas, which successively allot new equilibria to the sorption process.

TABLE V. MOISTURE REGAIN OF WOOD PULP SHEETS AT 25° C.

SAMPLE	25% R. H.[a]	50% R. H.	75% R. H.	100% R. H.	LIQUID WATER
	%	%	%	%	%
Free pulp	3.5	6.0	9.3	24.8	154
"Hydrated," dried from water	(2.4)	6.2	9.5	25.3	60
"Hydrated," but dried from alcohol	3.6	6.3	9.7	26.8	206

[a] Relative humidity.

It is concluded, in agreement with other investigators (*2*), that the so-called "hydration" of paper pulps has nothing to do either with a chemical hydration of cellulose, or with any form of surface or volume sorption by the fibers. It appears to be rather a name for a complex of phenomena depending upon the grosser mechanical dispersion of the fibers (including fibrillation) whereby water in the mass is mechanically subdivided in greater degree and has to drain, under given hydrostatic head, through a greater number of finer and more complex channels. So far as the change in mechanical properties of the sheet with beating are concerned, they appear to be well discussed and satisfactorily accounted for by Campbell (*2, 2A*).

One aspect of water retention by colloidal materials which perhaps deserves a note in this connection is the fact that certain colloid systems apparently brought to equilibrium at 100 per cent relative humidity will take up considerably more water in liquid water. It is called von Schroeder's paradox, since this investigator drew attention to it in connection with gelatin (*22*). It is not possible to discuss here the controversy about the reality and nature of this phenomenon (*6*). The argument that equilibrium has not been attained at 100 per cent relative humidity (saturation) does not meet the fact of the enormous discrepancy between certain materials admittedly saturated at 98 per cent relative humidity and soaked in liquid water. Nor does it meet the fact that it is elastic gels which show this behavior. Bancroft's explanation (*1A*), in terms of extra large or oversize pores (too large to condense water vapor), appears satisfactory *per se* but inadequate in two respects: It does not explain how such pores are formed by the swelling process itself, when they did not preëxist in the dry gel. (For if they did so exist, the gel—e. g., gelatin—would be opaque from light scattering.) Nor does he give an entirely satisfactory explanation of the retention of the extra water against gravitation and mechanical (centrifugal) drainage.

The writers have found that solvent swollen gels—cellulose xanthogenate, cellulose nitrate plus softener—coagulated in nonsolvent and then desolvated to give opaque xerogels, definitely show the greater sorption of liquid water. Here the cellular structure is clearly present. The production of it with transparent gels probably depends on the same process as hysteresis. In the primary adsorption, strains are released, and an internal cavitation is effected. If this extends to form cavities of sufficient size, we obtain the von Schroeder effect with liquid water.

The lower absorption and retention of liquid water by more translucent paper sheets from "hydrated pulp" has been noted. It is consistent with greater shrinkage on drying, and closer denser packing of the fibers so that the interfibrillar space is smaller.

Since this paper was completed, the authors' attention has been called to an important paper on "Some Chemical and Physical Observations on Hydration," by Kress and Bialkowsky (*10*).

LITERATURE CITED

(1) Astbury, W. T., *Trans. Faraday Soc.*, **29**, 193 (1933).
(1A) Bancroft, W. D., *J. Phys. Chem.*, **16**, 395 (1912).
(2) Campbell, W. B., IND. ENG. CHEM., **26**, 318 (1934).
(2A) Campbell, W. B., *Pulp & Paper Mag. Can.*, **29**, 185 (1930).
(3) Corey, A. B., and Gray, H. L., IND. ENG. CHEM., **16**, 853, 1130 (1924).
(4) Cross and Bevan, "Cellulose," 2nd ed., p. 4, Longmans, 1918.
(5) Davidson, G. F., *J. Textile Inst.*, **18**, T175 (1927).
(6) Freundlich, H., "Kapillarchemie," 2nd ed., p. 925, Akademische Verlagsgesellschaft m. b. H., 1922.
(7) Grace, N. H., and Maass, O., *J. Phys. Chem.*, **36**, 3046 (1932).
(8) Katz, J. R., *Kolloidchem. Beihefte*, **9**, 1 (1917); *Physik. Z.*, **25**, 321 (1924).
(9) Katz, J. R., and Samwel, P., *Ann.*, **472**, 241 (1929).
(10) Kress and Bialkowsky, *Paper Trade J.*, **93**, 35–44 (1931).
(11) Mathieu, M., *Trans. Faraday Soc.*, **29**, 122 (1933).
(12) Meyer, K. H., and Mark, H., "Aufbau der hochpolymeren Substanzen," Hirschwaldsche Buchhandlung, Berlin, 1930.
(13) *Ibid.*, p. 125.
(14) Miles, F. D., *Trans. Faraday Soc.*, **29**, 110 (1933).
(15) Miles, F. D., and Craik, J., *J. Phys. Chem.*, **34**, 2607 (1930).
(16) Neale, S. M., *Trans. Faraday Soc.*, **29**, 228 (1933).
(17) Newsome, P. T., and Sheppard, S. E., *J. Phys. Chem.*, **36**, 930 (1932).
(18) Northrop, J. H., and Kunitz, M., *J. Gen. Phys.*, **10**, 161 (1926); **13**, 565 (1930).
(19) Oguri, S., *J. Soc. Chem. Ind. Japan*, **35**, 235B (1932).
(20) Peirce, F. T., *J. Textile Inst.*, **20**, T133 (1929).
(21) Pidgeon, R. M., and Maass, O., *J. Am. Chem. Soc.* **52**, 1053 (1930).
(22) Schroeder, P. von, *Z. physik. Chem.*, **45**, 75 (1903).
(23) Seborg, C. O., and Stamm, A. J., IND. ENG. CHEM., **23**, 1271 (1931).
(24) Sheppard, S. E., *Trans. Faraday Soc.*, **29**, 77 (1933).
(25) Sheppard, S. E., and Keenan, R., *Nature*, **121**, 982 (1928); Keenan, *J. Phys. Chem.*, **33**, 371 (1929); Sheppard, Keenan, and Nietz, IND. ENG. CHEM., **21**, 126 (1929).
(26) Sheppard, S. E., and Newsome, P. T., *J. Phys. Chem.*, **33**, 1817 (1929).
(27) *Ibid.*, **37**, 389 (1933).
(28) Speakman, J. B., *Trans. Faraday Soc.*, **29**, 148 (1933).
(29) Stamm, A. J., *J. Phys. Chem.*, **33**, 404 (1929).
(30) Trillat, J. J., *Compt. rend.*, **191**, 654 (1930).
(31) Trogus, C., Tomonari, T., and Hess, K., *Z. physik. Chem.*, **16B**, 351; **17B**, 241 (1932).
(32) Urquhart, A. R., *J. Textile Inst.*, **20**, T117, T125 (1929).
(33) Urquhart, A. R., and Williams, A. M., *Ibid.*, **15**, T138 (1924).

RECEIVED May 20, 1933. Presented before the Division of Cellulose Chemistry at the 85th Meeting of the American Chemical Society, Washington, D. C., March 26 to 31, 1933. This paper is Contribution 520 from the Eastman Kodak Research Laboratories.

BY-PRODUCT NITROGEN PRODUCERS IN GERMANY recently consummated a modified agreement regarding the position of their output in the total national nitrogen output controlled by the German Nitrogen Syndicate.

Under the syndicate agreement heretofore in force, coke producers were allotted a normal production quota of 92,000 tons of nitrogen annually. However, actual sale of this quota was regulated by the degree of utilization of the total quota for the entire syndicate, including the synthetic producers. Since, during the past year, the syndicate was able to utilize only 30 per cent of the normal quota, the coke producers would be entitled to an output, without payment of any penalty, of 30 per cent of their normal quota, or approximately 27,600 tons. However, coke-oven ammonia occurring as an uncontrollable by-product has actually been running around 55,000 tons a year, and since the coke producers have insisted upon disposing of this output, an arrangement was set up whereby they might pay indemnity to the synthetic producers for their sales above the 30 per cent, which indemnity has run between 2 and 4 pfennigs per kilogram of nitrogen. This situation was highly unsatisfactory to the coke producers, and they indicated their desire to withdraw from the syndicate. The modified agreement provides for the sale of the entire output by the coke plants but penalty for exceeding the average utilization of the entire syndicate, which they must pay to the synthetic producers, will be appreciably reduced. The continued effective regulation of market conditions and avoidance of friction between the two groups of cokery and synthetic producers are thus assured to July 1, 1935.

Analytical Constants of Peanut Butter

Helen L. Wikoff, Maribodine Busey, and A. M. Kaplan
The Ohio State University, Columbus, Ohio

PEANUTS have been used as a food for two or three hundred years. The high calorific value of the oil and the protein content of peanuts make them a cheap and nourishing article of diet. Recent work tends to show the presence of vitamins in peanuts.

However, the whole peanut often proves rather indigestible because the nut meats are not broken into small enough particles in the process of chewing. For this reason the product consisting of finely ground nuts known as peanut butter has become a foodstuff of increasing importance, while the whole nuts are eaten chiefly as a confection.

Although peanut butters have been manufactured for a number of years, little information concerning their analytical constants is available. No standards for the composition of peanut butter have been established by the Government. Therefore a study of the analytical constants of samples purchased on the market was made to determine whether variations exist between products prepared by different manufacturers and whether adulterations can be readily detected.

Experimental Procedure

Moisture was determined by drying 10-gram samples of peanut butter to constant weight in an electric oven at 100° C. Ash was determined by carefully charring these dried products and igniting to constant weight. These residues, reignited after washing with 10 per cent hydrochloric acid, comprised the acid-insoluble ash.

The ether-soluble substances (the oil) were extracted from dried samples with dry ether in a Soxhlet apparatus for 15 to 20 hours. The insoluble residue left after boiling the fat-free meal successively with 1.25 per cent sodium hydroxide and 1.25 per cent sulfuric acid consisted of crude fiber. This fat-free meal was also used for determining the protein content by the Kjeldahl method. Chlorides were determined by the usual Volhard procedure, using aliquot portions of the filtrate prepared by heating samples of peanut meal to boiling in measured volumes of distilled water.

Samples of meal were digested in alcohol, and tests were made for reducing substances in the filtrate with alkaline copper tartrate solution. Total reducing substances were calculated as glucose after hydrolyzing the meal with hydrochloric acid on a boiling water bath. The amount of copper oxide formed by the reduction of the alkaline copper tartrate solution was determined volumetrically according to the Shaffer-Hartmann method.

The starch present in the meal was liquefied and partially hydrolyzed by a solution of diastase (102° Lintner) prepared from barley malt. Hydrochloric acid was used to bring about complete hydrolysis after the insoluble matter had been filtered from the solution. The glucose resulting was determined by the Shaffer-Hartmann method, and the starch calculated by use of the factor 9.4.

The pentosans in the meal were converted to furfural by the standard method of distillation with 12 per cent hydrochloric acid. The furfural was then determined volumetrically by the excess bromine method (*1*), and the pentosans calculated by the use of Krober's tables.

Discussion of Results

Moisture. The average amount of moisture found in the peanut butters examined was 1.74 per cent, while individual brands varied from 0.87 to 3.7 per cent. The highest moisture content was found in an unroasted brand of peanut butter. Measured amounts of water were incorporated into one of the butters studied, and it was found that the only visible effect produced by the addition of small quantities of water was a stiffening of the product. As much as 20 per cent water could be added without seriously changing the appearance of the peanut butter, but these products spoiled rapidly.

Ash. The ash content of the ten brands of butter varied from 1.91 to 3.18 per cent with an average value of 2.37 per cent (dry basis). The acid-insoluble ash varied from 0.07 to 0.25 per cent. As this figure is a measure of silicates, grit, and other acid-insoluble matter, the peanut butters examined seem to have been made from a clean quality of nuts.

Chlorides. Salt is usually added to peanut butter for seasoning, and the amount depends upon the taste desired. Heinz peanut butter, known by its salty taste, yielded a dry meal containing 3.45 per cent sodium chloride although the average amount of chlorides in all samples was 1.60 per cent on the basis of the dry meal.

Oil. The percentage of oil in the peanut butter samples varied more widely than any other constant determined. The range was from 39.45 to 52.34 per cent with an average value of 46.70 (dry basis). This difference in the oil content is probably due to the varieties or mixtures of peanuts used in the manufacture of the butter. Virginia varieties of peanuts make a dry gritty product while the Spanish nuts are very oily (*2*). Usually one part of Spanish nuts is mixed with three parts of Virginia nuts, or equal parts of each may be used. The manufacturer of one sample of butter with a high oil content added corn oil to the nuts before grinding in order to make the salt adhere.

Refractive Index. The refractive index of peanut oil is normally from 1.471 to 1.474. Values for the oils obtained from this series of peanut butters ranged from 1.4540 to 1.4749 with an average value of 1.4676.

Table I. Analyses of Peanut Butters and Meals

	Beech-nut	Chapman Unroasted	Heinz	Battle Creek Unroasted	Chapman Roasted	Premier	Franklin's Uncle Ben	Franklin Highest Quality	Capitol	Frank's Jumbo	Average	Per Cent Whole Sample as Purchased
Refractive index of oil	1.4651	1.4730	1.4540	1.4631	1.4669	1.4682	1.4673	1.4740	1.4749	1.4690	1.4676	...
Moisture	2.01	3.72	1.46	1.34	3.13	1.70	0.88	1.09	1.24	0.87	1.74	1.74
Ash	3.03	2.38	3.18	2.33	2.27	2.31	1.91	2.22	2.11	1.95	2.37	2.33
Acid-insol. ash	0.12	0.07	0.17	0.16	0.16	0.08	0.21	0.25	0.24	0.25	0.17	0.17
Oil	47.88	48.15	48.34	48.87	52.34	39.45	46.78	41.68	46.54	46.96	46.70	45.89
					PEANUT MEALS							
Protein	58.84	59.12	56.38	62.45	59.43	54.64	59.31	56.43	61.26	58.59	58.65	30.72
Chlorides	1.76	1.08	3.45	1.50	1.51	1.17	1.43	1.12	1.54	1.73	1.60	0.84
Total reducing substances calcd. as glucose	28.29	26.62	26.67	24.66	28.95	29.92	23.37	24.28	22.77	26.54	26.21	13.73
Crude fiber	3.58	3.38	2.87	3.33	3.46	3.46	2.99	3.36	2.67	4.31	3.34	1.74
Starch	19.32	18.55	18.39	16.12	20.82	21.43	15.70	16.43	14.46	17.87	17.91	9.38
Pentosans	5.95	6.81	6.11	5.56	6.74	6.20	5.13	6.17	5.30	6.06	6.00	3.14

Crude Fiber. Crude fiber is essentially a measure of the cellulose content. The average value for the ten brands of meal was 3.34 per cent, varying from 2.67 to 4.31 per cent. This should be a valuable determination in case of adulteration with shriveled or dry nuts, or vegetable products such as shells, roots, and stems.

Protein. The protein in the dry meal examined varied from 54.64 to 62.45 per cent with an average value of 58.65 per cent. This is equivalent to about 30 per cent (30.66) on the basis of the whole butter.

Reducing Substances. Qualitative tests showed the absence of reducing sugars before hydrolysis. Starch cellulose and pentosans were the polysaccharides found in the fat-free meal. After the hydrolysis, the reducing sugars calculated as glucose ranged from 22.77 to 29.92 per cent (average 26.21) on the basis of the dry meal. This range in values was chiefly due to differences in starch content (14.46 to 21.43 per cent with an average value of 17.91). The amounts of pentosans, 5.30 to 6.81 per cent, varied less than one per cent from the average, 6 per cent.

Literature Cited

(1) Kline, G. M., and Acree, S. F., *Bur. Standards J. Research*, 8, 25–35 (1932).

(2) Thurston, "Pharmaceutical and Food Analysis," p. 172, Van Nostrand, 1923.

Received September 10, 1932. Presented in part before the Division of Agricultural and Food Chemistry at the 84th Meeting of the American Chemical Society, Denver, Colo., August 22 to 26, 1932.

Vitamin C Content of Canned Tomato Juice

Ray G. Daggs and A. G. Eaton, Department of Vital Economics, University of Rochester, Rochester, N. Y.

Tomato juice has fast become a widely popular drink and has been highly recommended because of its vitamin content. The present report is part of a study of the vitamin content of a local commercially canned tomato juice and is intended as a demonstration of the fact that the tomato juice tested can be put up without suffering loss of vitamin C in the process of canning. It is also desired to emphasize the technic of assay.

There has been a considerable amount of work done on the vitamin content of raw tomatoes, strained tomatoes, tomato juice extracted in the laboratory, and cooked tomatoes, but very little on the vitamin C content of commercially canned tomato juice. Kohman, Eddy, and Gurin (*4*) have recently published an article on the canning of tomato juice without vitamin C loss in which they have incorporated what they term a "composite test" of five of the most popular brands of commercial tomato juice. They compare three batches of experimental juice with canned tomatoes, sieved canned tomatoes, and the composite of five commercial tomato juices. Doses of 3 and 5 cc. were fed, and two or three animals were used in each group. Concerning the five commercial juices (fed in succession in 5-day intervals), they state: "Of the six guinea pigs receiving the commercial tomato juice, only one animal on the 5-cc. dosage was free from scurvy symptoms. . . . The four animals receiving canned tomatoes were entirely free from scurvy symptoms, while the guinea pigs on the 3-cc. dosage of the juice made by sieving canned tomatoes had no more than dubious symptoms of scurvy." Three cc. of canned tomatoes were protective and 3 cc. of the juice made by sieving canned tomatoes were nearly protective against scurvy, while 5 cc. of commercially canned tomato juice did not protect.

Some workers attach rather great importance to the growth curves of guinea pigs in a vitamin C assay. The writers believe this to be a fallacy. There is little evidence to show any specificity of vitamin C for growth such as is found for vitamin B_4. Growth is a complex phenomenon and is dependent upon many factors, and therefore cannot in itself be used as a criterion for any one. It is true that Sherman incorporated the growth curve in his assay method but only as a help in the interpretation of the results. Sherman distinctly points out the individual variation in the growth curves and places the major emphasis on the autopsy findings. Eddy (*1*) in a study of the vitamin C content of string beans shows growth curves of tremendous variability. For example, animal 9 on 18 grams of beans showed a gain of only a little over 100 grams in 90 days while animal 8 on only 12 grams of beans showed a gain of about 400 grams for the same period. The main thesis of the paper, however, is devoted to a comparison of the Sherman method with that of Höjer (*2*). Eddy presents evidence from his own studies of the validity of the Höjer method and states that it is a much more sensitive one than the Sherman scoring system.

Höjer (*2*) states that Sherman's method often gives variations of 100 per cent or more in determining the fully protective dose. Höjer introduced an assay method of his own that is dependent upon the pathological changes in the tooth picture. He states that his method is just as good as that of Sherman and that single animals may diverge a good deal from the others of the same group. He recommends the use of "several" animals in each group.

Until such a time as we have a practical quantitative method for the estimation of "ascorbic" acid, the writers believe that Sherman's method of assay must be carried out on at least five to ten animals per group with the tabulation of autopsy findings in order to justify in the slightest measure the drawing of even suggestive conclusions. The Höjer method also must be carried out on several animals in order to rule out the individual variations that Höjer himself admits exist. Workers in the vitamin field are too prone to draw sweeping conclusions from too few experiments.

The following experiments are short, but we feel that they are quite conclusive, especially in light of the work that has been done on canned tomato juice.

Experimental Procedure

Guinea pigs, weighing from 200 to 300 grams, were divided into groups of seven each, according to weight and sex. Each guinea pig was placed in a separate screen-bottomed cage and supplied with distilled water from a glass cup. The basal ration was fed ad libitum, and 20 grams of fresh cabbage were supplied daily for the first week in order to accustom the animals to the cages and the ration, and to some extent to standardize the stores of vitamin C.

The basal ration consisted of the following parts:

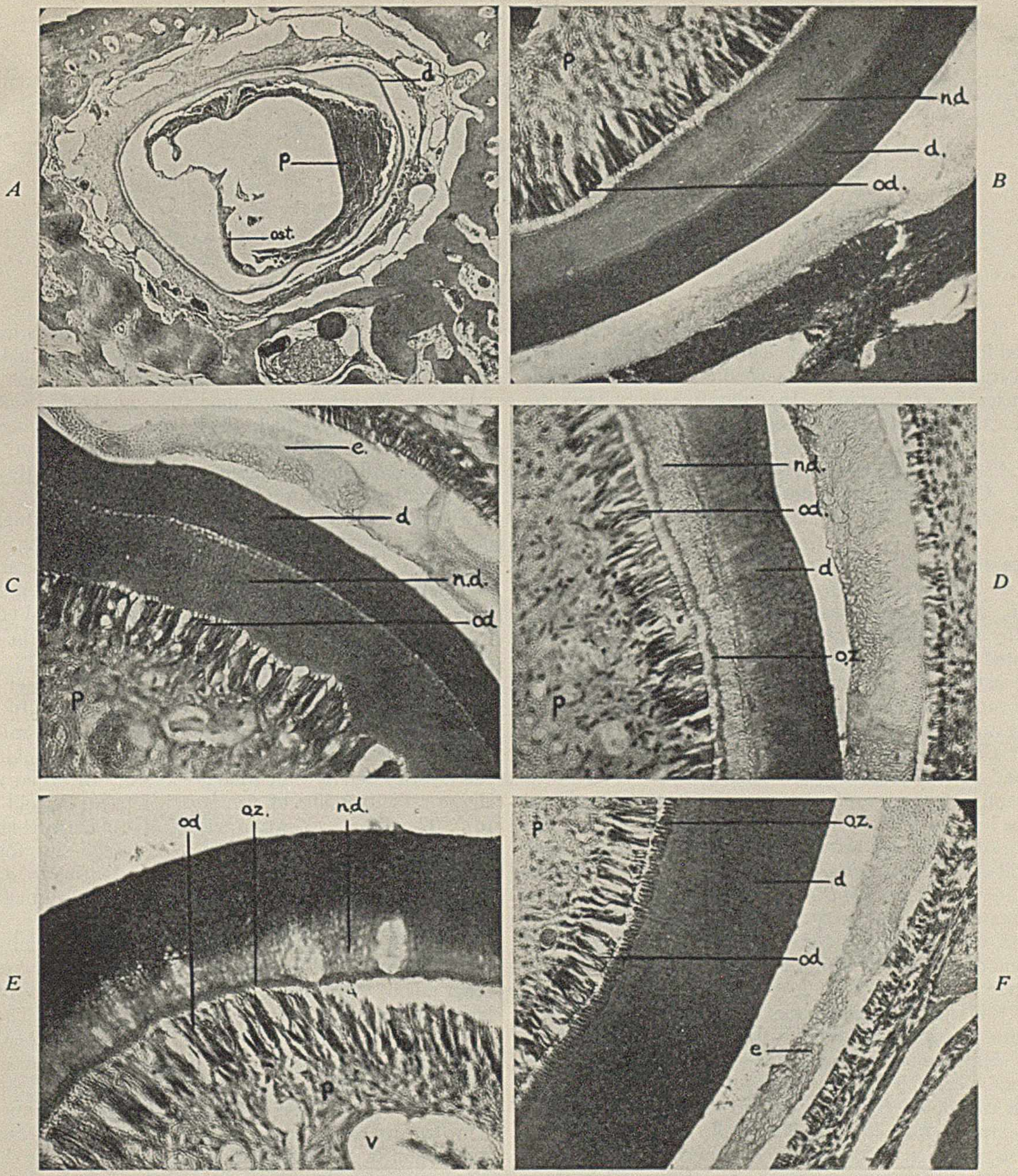


Figure 1. Pathological Findings in Teeth Examinations

p.	Pulp	*n. d.*	New dentine	*o. z.*	Odontogenic zone
d.	Dentine	*od.*	Odontoblasts	*v.*	Vacuolation
ost.	Osteodentine	*e.*	Enamel		

Rolled oats (ground)	29.5
Wheat bran	29.5
Skim milk powder (heated in shallow trays at 110° C. for 3 hours, stirred each hour)	30.0
Butter fat (freshly churned)	9.0
Sodium chloride	1.0

Fresh Patch's cod liver oil was administered daily by pipet. The ration was mixed in small batches once a week and stored in the ice box.

At the end of the first week the cabbage was withdrawn and graded doses of tomato juice were given, as indicated in the tables. The tomato juice was administered daily directly into the mouth by pipet, as preliminary trials showed that the animals would not consume the juice readily enough from cups to prevent the loss of vitamin C by oxidation.

Weights were recorded daily in order to obtain some information as to the general conditions of the animals as the experiment progressed. The experimental period was 60 days, at the end of which time all pigs surviving were chloroformed and autopsied according to the method of Sherman, LaMer, and Campbell (*5*), and the degree of scurvy was expressed numerically by adding up the plus signs.

It is generally customary to run vitamin C assays a little longer than this, but, since it was desired to make a direct comparison of the canned tomato juice with the fresh field-ripened tomatoes from which the juice was made, it was necessary to shorten the experimental period. The writers consider a direct comparison with fresh tomatoes of far more importance than the few extra days of experimental feeding.

All of the tomatoes were of the John Baer variety. The

TABLE I. NEGATIVE CONTROLS[a]

Time Required to Show Signs of Sore Joints	Duration of Life	Bony Structure				Hemorrhages				Score (Sum of + Signs)
		Jaws	Teeth	Ribs	Joints	Ribs	Intestines	Joints	Muscles	
Days	*Days*									Score
17	23	+++	?	+++	+++	+++	+++	+++	+++	21
19	25	+++	?	+++	+++	+++	+++	+++	+++	21
15	23	+++	?	+++	+++	+++	+++	+++	+++	21
17	24	+++	?	+++	+++	+++	+++	+++	+++	21
22	24	+++	?	+++	+++	+++	+++	+	++	18
20	31	+++	?	++	+++	++	+++	+++	+++	19
23	34	+++	+++	+++	+++	+++	+++	+++	++	23
Av. 19	26									20.5

[a] Most of the animals did not live long enough to show major macroscopic tooth changes, loosening, etc.

canning of the juice began in the last week of August and continued into the third week of October, the tomatoes being supplied fresh daily. This time lacked about 10 days of the 60-day experimental period. In order to supply fresh tomatoes for these last 10 days, a large number of tomatoes from the last few days of picking were individually wrapped in paper and stored in the ice box at a temperature a little above freezing. Choice, firm, nondeteriorated, nonfrozen tomatoes were selected daily from these stored tomatoes for the experiment.

The canned tomato juice was prepared in the following manner at the packing house: The tomatoes were washed, and firm, well-ripened ones were selected, cored, and extracted by a screw-type tomato juice extractor. The juice was heated in vacuum (below pasteurization temperature) and the cans were filled under vacuum. (The 1932 pack was not canned under vacuum but was heated in vacuum.) After the cans were sealed, they were pasteurized, labeled, and packed. Cans from each day's pack were taken to the laboratory and used for that day's feeding.

The fresh tomatoes were brought to the laboratory and kept in the ice box for a few hours before extracting. The tomatoes were cored and pressed through a kitchen sieve by hand while still cold. This extracted juice was immediately centrifuged in order to express the air and was fed at once. This fresh tomato juice compared favorably in color and consistency with the canned juice, the only difference being a finer suspension of pulp in the canned juice owing to the use of a finer extracting screen.

All of the autopsies were performed by the same person. The results are summarized in Tables I and II. The sum of the plus signs is shown as an index of the degree of scurvy. The actual Sherman score as suggested by Kenny (*3*) has not been calculated for those animals living less than the experimental period. Twenty-four is the maximum number of plus signs and indicates extremely severe scurvy. Only the averages of each group of seven animals are given, along with one illustrative table of the negative controls in order to show the method of tabulation.

In the canning of the 1932 pack the additional production of a vacuum during canning was eliminated. It was of some concern to learn whether or not this would appreciably alter the vitamin C content of the freshly packed juice. The 1932 juice was tested in the same manner as the 1931 juice, and Table II shows the average results.

TABLE II. AVERAGE SCORE OF PACKS OF TWO YEARS

	Fresh Juice Dose				Canned Juice Dose			
	1 cc.	2 cc.	3 cc.	4 cc.	1 cc.	2 cc.	3 cc.	4 cc.
1931 av. score	15.3	7.5	2.8	0	16.5	14.8	3.1	0.5
1932 av. score	..	5.1	2.1	.	..	8.5	3.0	...

When the animals of the 1932 experiment were autopsied, the lower jaws were carefully removed, cleaned, decalcified, and fixed, and histological sections were made of the incisors. The sections were carefully examined, the procedure being essentially that of the Höjer method (*2*) with the exception that the animals had been on experiment 60 days instead of the usual 2 weeks. (Höjer suggests that the method may be "made sharper by letting the animals live longer than 2 weeks.") No attempt was made to score the findings according to the Höjer method. The pathological findings in the teeth offered an additional check on the vitamin C content of the tomato juice. Figure 1 gives characteristic findings for the different groups of animals.

Figure 1*A* shows a complete cross section of a lower incisor of a guinea pig receiving no tomato juice and dying of scurvy in 29 days. The pathological examination reveals an almost complete disintegration of the pulp tissue and the presence of only a thin band of dentine bounded on its pulpal border by a layer of osteodentine. The disappearance of the odontoblasts is typical of complete scorbutus.

The remaining photographs are of slightly greater enlargement and show only a part of the cross section. In *B* (2 cc. fresh juice) the odontoblasts are shown to be present but are shortened and irregular in appearance. The pulpal border of the layer of defective dentine is somewhat irregular and also shows a distinct line of demarcation from the old dentine (*d*). The defective dentine is indicative of faulty calcification because of the lack of fusion of the calcospherites formed by the odontoblasts. The inner layer of dentine (*n. d.*) unlike the outer layer of older dentine (*d*) lacks the normal tubular appearance of true dentine.

Figure 1*C* (2 cc. canned juice) presents conditions similar to those found in *B*. There is, however, a slightly greater disorder among the odontoblasts and a greater degree of irregularity of the pulpal border of the new dentine. The degree of difference between *B* (2 cc. fresh juice) and *C* (2 cc. canned juice) can hardly be considered significant because such a difference occurs as individual variation within the group.

Figures 1*D* (3 cc. fresh juice) and *E* (3 cc. canned juice) show similar tooth pictures. There is a slightly greater disintegration in the canned than in the fresh. As the higher doses are reached, the distinct line of demarcation between the two dentine layers is lacking, and they tend to merge one into the other. There is still some engorgement of the blood vessels and vacuolation in the pulp and irregularity of the odontoblasts.

Figure 1*F* is taken from a group receiving 5 cc. of canned juice and is illustrative of a practically normal tooth picture. The dentine has the normal tubular appearance. The laminations of the dentine do not indicate an abnormal condition. The slight irregularity of the odontoblasts shown in this particular section is probably due to tearing during sectioning.

DISCUSSION OF RESULTS

Table I shows that the negative controls developed scurvy on the average at 19 days and died at 26 days. In the 1931 pack, 4 cc. of fresh or canned juice were necessary to afford complete protection, but 3 cc. of the canned as well as the fresh juice gave very low scurvy scores. Only in the 2-cc. groups is the canned juice distinctively less protective than the fresh, and the wide difference here might well be due to animal variation. No such variation occurred in the 2-cc. group for the 1932 pack or in any of the other dosages. The 1-cc. group shows only a slightly higher score for the canned juice. It is clearly evident that there is a slight destruction of vitamin C in the canned juice in the process of packing, but this is slight indeed when one considers the ease with which the vitamin is oxidized.

It is evident from Table II (1932 pack) that sealing the cans under an additional mechanical vacuum is not essential. The results show slight destruction of vitamin C in the canned juice, but it is of about the same order of magnitude as in the 1931 test.

The tooth sections confirm the findings of the Sherman method for the 1932 pack and serve as an additional check on the vitamin C content of the canned tomato juice as compared with the fresh.

The work indicates only a slightly lower content of vitamin C in this particular brand of commercial tomato juice as compared with the fresh tomatoes from which the juice was commercially extracted. The authors do not wish to imply by this study that all brands of commercially canned tomato juice are satisfactory in vitamin C content just because this one brand proves so. There are undoubtedly many inferior products on the market. Neither do they want the reader to infer that the brand tested here is the only satisfactory brand available.

ACKNOWLEDGMENT

The sections of the incisors of the animals in the 1932 experiments were examined by C. D. M. Day, Rockefeller Dental Fellow in the Department of Vital Economics, University of Rochester.

LITERATURE CITED

(1) Eddy, W. H., *Am. J. Pub. Health*, 19, 1309 (1929).
(2) Höjer, A., *Brit. J. Exptl. Path.*, 7, 356 (1926).
(3) Kenny, C. L., Dissertation, Columbia University, New York, 1926.
(4) Kohman, E. F., Eddy, W. H., and Gurin, C. Z., IND. ENG. CHEM., 25, 682 (1933).
(5) Sherman, H. C., LaMer, V. K., and Campbell, H. L., *J. Am. Chem. Soc.*, 44, 165 (1922).

RECEIVED July 31, 1933.

The Keeping Quality of Frozen Orange Juice

M. A. JOSLYN AND G. L. MARSH, University of California, Berkeley, Calif.

A study of factors that influence the keeping quality of frozen orange juice stored over 2 years at 0° F. (−17.8° C.) has been made, and the results are here reported.

THE permanent and complete preservation of orange juice is rendered difficult by the complex nature of the changes occurring after extraction of the juice from the fruit. The chief undesirable changes in flavor are the development of bitterness, and formation of stale, limey, musty, or terpeney tastes, or flatness owing to complete loss in flavor. In addition, browning or discoloration commonly occurs. Investigations reported by Creuss (*3*), McNair (*11*), Joslyn (*8*), and Camp et al. (*1*), as well as common commercial experience in California, have demonstrated that the maturity of fruit markedly affects the extent and kind of change in flavor. McDermott (*10*) found that the darkening and, to some extent, undesirable changes in flavor of pasteurized Florida orange juice at room temperature were caused chiefly by oxidation. He demonstrated that the darkening could be prevented and changes in flavor retarded by evacuating the juice and sealing under vacuum or replacing the air dissolved in the juice as well as that in the head space above with an inert gas. Similar results were obtained by Gore (*4*) and Matthew (*9*). It is also known (*4, 6, 9*) that discoloration of pasteurized orange juice can be almost completely inhibited by storage at low temperatures.

Although the deterioration of orange juice is due in great part to oxidation, it does not depend entirely on this cause. Deterioration in flavor is not always accompanied by darkening of the color. The color of orange juice may be successfully preserved by cold storage or by reducing oxidation of pasteurized juice to a minimum; but deterioration in flavor is not entirely prevented by such treatment. Chace and Poore (*2*), Gore (*4*), Irish (*6*), Joslyn (*7, 8*), and Turnbow and Cruess (*13*), as well as others, resorted to freezing storage as the most satisfactory means of preservation. However, as pointed out by Joslyn (*8*), undesirable changes in flavor have occurred in untreated juice even at 0° F. (−17.8° C.).

EXPERIMENTAL PROCEDURE

VARIETY AND SOURCE OF FRUIT. In the majority of the experiments it was necessary to prepare uniform samples of juice to be treated in various ways from fruit of known history. Valencia oranges grown at the University of California Citrus Experiment Station at Riverside were used in most of these tests, although Orange County fruit was also used. For studies on the effect of fruit maturity on the keeping quality of the juice, representative samples of Valencia oranges were picked periodically at Riverside and expressed to Berkeley where they were used immediately after arrival. Washington navel oranges picked periodically at Riverside and at an orchard in Thermalito, Butte County, and shipped by express to Berkeley were also used in studies on the effect of maturity. Maturity studies were made during the seasons of 1931 and 1932.

Fruit of approximately the same size was used, since a preliminary investigation had shown that a marked variation of composition with size occurred in choice Valencia oranges picked at the same time from the same grove.

METHOD OF EXTRACTION. The fruit was washed and burred on a revolving straight-ribbed conical extractor. Care was taken to minimize exposure of the halved fruit to the air and, by using only moderate pressure when burring, to incorporate as little as possible of the albedo. About 2 liters of juice were generally burred for each test. The juice was strained through cheesecloth at first and in later tests through an aluminum screen having eighty 1-mm. holes per square inch (6.5 sq. cm.).

It was later found that the juice absorbed a slight odor from the cheesecloth, and this practice was discontinued in favor of straining through a perforated aluminum screen. The time of burring and subsequent straining in this manner varied from 2 to 5 minutes.

Directly after straining, the juice was thoroughly mixed and the temperature recorded. This varied from 65° to 72° F. except for juice from precooled fruit, in which the temperature was considerably lower.

Deaërating the Juice. In some of the early tests the juice was subjected to the highest vacuum obtainable in an aspirator pump for 10 minutes; however, in order to standardize this procedure, 800 to 1000 cc. of the juice were exposed to a vacuum of 28.75 inches (73 cm.) for a period of 10 minutes after this point was reached. The time to reach this degree of vacuum varied from 2 to 3 minutes. The juice, at room temperature, began to foam and bubbles of gas to form in the interior when a vacuum of 27 inches (68.6 cm.) was reached; below this vacuum the deaëration did not cause any apparent effect on juice at room temperature. During deaëration the bottle was shaken several times to aid removal of gases from the juice. At the end of this period, the vacuum was relieved with air, unless otherwise stated, and the juice filled into the storage containers.

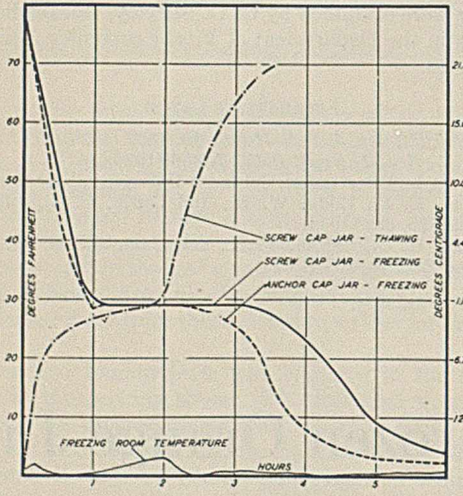


Figure 1. Temperature Changes in Orange Juice in 4-Ounce (120-cc.) Glass Containers during Freezing at About 0° F. (−17.78° C.) and Thawing at Room Temperature at About 68° F. (20° C.)

Containers. Four-ounce (120-cc.) wide-mouthed crown-cap glass jars, 4-ounce screw top, and anchor cap jars were used. The glass containers were chosen in order to permit observation of the juice during freezing and subsequent thawing, and because they were neutral to the juice. All containers were sealed at atmospheric pressure unless otherwise stated.

Storage Conditions. Immediately after sealing, the containers, filled to about 90 per cent of their volume with juice, were stored in the freezing room at about 0° F. (−17.8° C.). They were generally solidly frozen within 3 hours after storage. Temperature changes as measured by thermocouples and potentiometer during freezing and subsequent thawing at room temperature are shown in Figure 1. Temperature changes in the center of the anchor cap jar were but slightly different from those in the center of the screw cap jar. The storage temperature fluctuated from 2° to 6° F. (1.1° to 3.4° C.) at first although in one instance the samples were subjected to a temperature of about 20° F. (−6.7° C.) for over a week.

Examination of the Juice. Six samples of juice, as nearly alike as possible, were prepared for each test and stored as above. At certain intervals during the course of storage, samples were removed for examination. These were allowed to thaw for about 3 hours at room temperature. The appearance of the juice, settling of pulp, clumping of pulp, etc., were noted, and the samples were shaken, opened, and tasted. Independent observations as to flavor of the juice were made by at least two individuals. It was found by practice that a critical tasting ability could be developed so that even slight differences in taste could be detected. The results of observations by other tasters generally agreed with those made by the authors. No more samples than could be comfortably tasted were removed at one time, and the sampling was spread over a period of several days. Duplicate samples were so alike in appearance and flavor that in most cases single samples were tasted except in case of doubt, and then duplicates were examined. The frozen samples were removed for observation after about 2, 7, and 13 months storage.

Analysis of Juice. In an attempt to find a correlation between gross composition and keeping quality of the juice, the specific gravity, total titratable acidity, and, for certain samples, the iodine number of the juice were determined as follows; all analyses were made in duplicate and repeated if closely agreeing results were not obtained: The acidity expressed as per cent citric acid was determined by titrating in the hot with phenolphthalein as indicator. The specific gravity of the juice was determined by means of a chainomatic Westphal balance with an accuracy of about 0.0002; from the specific gravity the Balling degree was determined from the Association of Official Agricultural Chemists official sugar tables and corrected for temperature to 20° C. The ratio of total soluble solids or Balling degree to acidity was calculated and expressed as ratio.[1]

The iodine number of the juice was determined by titrating a 50-cc. sample of the juice with 0.01 *N* iodine solution in the presence of a few cubic centimeters of a 1 per cent starch solution. According to Szent-Györgyi (*12*), "the end point in the titration is reached when the reduction of iodine becomes suddenly very slow." The end point chosen was that at which the dull brownish blue color of the starch persisted for about 15 or 20 seconds. The volume of 0.01 *N* iodine solution required to titrate 50 cc. of juice is designated as the iodine number.

As was to be expected, the specific gravity of undeaërated juice, because of the gases present, was appreciably lower than that of the deaërated juice, being 0.3 to 0.6 lower in degrees Balling.[2] After freezing and subsequent thawing there was no appreciable difference between the specific gravity of the deaërated and untreated juices. The acidity of the untreated juice which, because of its lower specific gravity, was expected to be somewhat lower than that of deaërated juice, was lower in some cases and higher in others, owing, perhaps to poorer end point and lack of uniformity in sampling. There was no appreciable difference in titratable acidity between fresh and frozen juice and also no appreciable difference in the iodine number.

The Keeping Quality of Frozen Orange Juice

Appearance. In all cases it was found that, after thawing, the pulp in undisturbed samples settled in deaërated juice but was partially suspended and partially settled in undeaërated samples. The separation of the pulp was

---

[1] It is the practice to express the ratio of soluble solids to the acid naturally existing in the fruit as the ratio of Balling degree to per cent acid as anhydrous citric acid. This is only approximately equivalent to the sugar-acid ratio which is also used. The ratio of Balling degree to per cent citric acid is commonly called "ratio" and given as such in the literature—for example, Baier, W. E., and Higby, R. H., *Calif. Citrograph*, **16** (5), 202, 260 (1931).

[2] The difference between specific gravity of plain and deaërated juice depends on the time the burred juice is allowed to stand before testing. Upon standing, most of the air rises to the surface, and the specific gravity of the plain juice becomes practically equal to that of the deaërated juice.

appreciable after storage for one month and quite marked after 13 months. The separated pulp was only slightly clotted and curdled in appearance at first but became markedly clotted upon prolonged storage. The supernatant straw colored liquid in the deaërated juices and the middle portion of the untreated juices were brilliantly clear and free from suspended colloidal particles.

Flash pasteurization at 165° to 185° F. (72° to 85° C.) prior to freezing did not prevent the separation and clotting of pulp, but did prevent complete separation of suspended matter from the suspension medium. The large pieces of pulp settled in all cases whether the juice was deaërated or not prior to treatment, but the supernatant liquid remained cloudy. However, the chromatophores, to which the color and flavor of the juice are due in great part, settled, and the supernatant layer was straw-yellow in color and similar in appearance to centrifuged juice. Preliminary observations showed that clotting and separation of the pulp from the juice cannot be entirely prevented by more rapid freezing, as reported by Camp et al. (*1*).

No apparent change in color other than that caused by the separation and clotting of pulp occurred during freezing storage.

FLAVOR. Frozen orange juice subjected to oxidation during storage at 0° F. (−17.8° C.) deteriorated in flavor. A change in flavor was detectable after a storage period of 2 months and was quite marked after 6 months. The change in general was a decrease in orange flavor and aroma; the juice at first lost the fresh orange flavor and then progressively became flatter in taste until it finally lacked all orange flavor. The juice from immature fruit turned bitter and stale, even juice from mature fruit developed definite objectionable, stale flavors, in some cases. Deaërating the juice decreased the rate of loss in flavor even when the juice was exposed to air during storage. Closing the deaërated juice under vacuum, or under an atmosphere of inert gas, and especially precooling the fruit prior to extraction markedly decreased the changes in flavor during storage.

EFFECT OF DEAËRATION. To determine the effect of temperature and of vacuum, orange juice was deaërated under a vacuum of 28.75 inches (73 cm.) at 38°, 65°, and 80° F., (3.3°, 18.3°, and 26.7° C.), respectively; and juice at 70° F. (21.1° C.) was deaërated under vacuums of 15, 25, and 29 inches (38.1, 63.5, and 73.7 cm.), respectively. After storage for 62, 222, and 399 days it was found that the juice deaërated under the 29-inch vacuum was superior in flavor to that treated at lower vacuums. Although the juice deaërated at 80° F. retained more orange flavor than the rest, it had a slight off-flavor. It was found that the length of time which elapsed between extraction and freezing storage was of as much importance as the degree to which the gases present were removed. Untreated samples which were handled more promptly held up as well in storage as the treated samples. Subsequent tests, however, proved that deaërated juices retained their flavor more completely than untreated juices.

In the experiments described above, the vacuum applied during deaëration was relieved with air, and the deaërated juice was exposed to air during filling and storage. Tests were made to determine the effect of closing the jars under vacuum. Samples of untreated and deaërated juice were closed at atmospheric pressure and under a vacuum of 20 inches (50.8 cm.), respectively. It was found that closing under vacuum improved the keeping quality of both juices, but the improvement was more marked for untreated than for deaërated juice.

EFFECT OF TREATMENT WITH VARIOUS GASES. Small portions of juice were subjected to a vacuum for about 10 minutes, and the vacuum was then relieved by the introduction of carbon dioxide, oxygen, hydrogen, ordinary air, and oxygen-free nitrogen, respectively, below the surface of the liquid. The gas was bubbled vigorously through the juice for about one minute after the vacuum was relieved. Simultaneously with this series, these various gases were bubbled vigorously for a period of 5 minutes through portions of the same juices not previously treated in vacuum.

After storage for 2 months, the juices treated with oxygen-free nitrogen were found more nearly to have retained their original flavor; ordinary nitrogen was next best, then hydrogen; treatment with carbon dioxide resulted in a carbonated flavor which masked the orange flavor, but little loss in the orange flavor occurred; the oxygen-treated juice was flat and stale and much poorer in flavor than the untreated juice. After 7 months the nitrogen-treated juices were better in flavor than the rest. There was, however, but little difference between the juice treated with oxygen-free and ordinary nitrogen; the juice treated with carbon dioxide was next best, although it had less orange flavor than the nitrogen-treated juices; next in quality was the untreated juice, and last the oxygen-treated juice. The hydrogen-treated juice lacked orange flavor. After about 13 months of storage the order of desirability of the juices was nitrogen, hydrogen, carbon dioxide, untreated, and oxygen treated. After 20 months of storage the nitrogen-treated sample was markedly superior to the rest, the carbon dioxide being flat and somewhat off-flavor. The oxygen-treated sample was flat and stale. Similar results were obtained for the series in which the juice was treated with these gases at atmospheric pressure. The differences between the treatments was more marked in this series; thus the staleness of the oxygen-treated samples was more marked and so also was the difference between nitrogen-treated and other samples.

A comparison of helium, nitrogen, carbon dioxide, and air treatment with untreated juice was made using several lots of Valencia juice. It was found that the helium-treated was about equal to the nitrogen-treated juice; the juice treated with carbon dioxide was carbonated in flavor and did not retain nearly as much orange flavor as the nitrogen-treated; the hydrogen-treated juice was poorer in flavor than the nitrogen-treated; the air-treated juice was flatter in flavor than the untreated which tasted somewhat stale.

EFFECT OF OXIDATION. In order to determine the effect of exposure to air or oxygen upon the flavor and keeping quality of orange juice, the following lots of juices were prepared: untreated, deaërated immediately after extraction, treated with oxygen for 5 minutes and then deaërated, treated with oxygen for 30 minutes and then deaërated, extracted from halved fruit exposed to air at room temperature for one hour prior to extraction. After 2, 7, and 13 months of storage the sample deaërated directly after extraction was markedly superior in flavor to the others. The samples treated with oxygen and not deaërated were stale and lacked flavor; those deaërated after oxygen treatment were of fresher flavor. The treated samples in general were sweet and devoid of orange flavor.

In order to increase the effect of oxidation, 25, 50, 100, and 500 p. p. m. of hydrogen peroxide were added. The juice became progressively flatter in flavor with increasing concentration of hydrogen peroxide and time of storage, but was not disagreeably objectionable in flavor. The iodine number of the juice decreased with increase in concentration of hydrogen peroxide, being for juice containing 0, 25, 50, 100, and 500 p. p. m. of hydrogen peroxide, respectively, as follows: 18.7, 13.6, 9.4, 3.4, and 1.3. The iodine number decreased slightly during storage. The added hydrogen peroxide did not affect the color of the juice at first. The juices containing 50 p. p. m. or over were gassy. The pulp was not bleached in color. After 13 months of storage, hydrogen peroxide had caused noticeable darkening of the juice. The darkening was perceptible at 50 p. p. m. and appreciable at 500 p. p. m. of hydrogen peroxide.

Effect of Orange Oil. In order to test the effect of orange oil on the keeping quality of Valencia orange juice, an orange oil emulsion was added to juice extracted from Riverside Valencias on August 21, 1931, so that the added oil content of the juice was 0.005, 0.01, 0.02, 0.05, and 0.10 per cent, respectively. Cold-pressed orange oil made by the California Fruit Growers Exchange was used in these tests. One portion of each lot of juice was deaërated after the addition of oil, and the other was untreated. In the fresh juice the presence of 0.005 per cent added oil could be readily detected by taste, and the flavor of the juice containing either 0.005 or 0.01 per cent oil was favored. The addition of orange oil changed the color of the juice from orange to yellowish orange, the amount of yellow increasing with the concentration of oil, confirming the results obtained by Camp et al. (*1*).

During storage for over 13 months the oil in both deaërated and nondeaërated series remained fresh in flavor and aroma and was not "terpeney." The addition of slight amounts of oil, about 0.005 per cent, gave a juice of fairly fresh orange flavor even after 13 months of storage, but 0.01 per cent was a little too strong in flavor. Even the addition of 0.005 per cent oil gave a product that was slightly more like orangeade than orange juice. Deaëration did not appreciably affect the stability of the added orange oil.

Effect of Amount and Kind of Suspended Matter. In order to determine the effect of various tissues, juice was prepared from Valencia oranges from Riverside on August 26, 1931, in a number of ways; samples consisted of burred juice, unstrained, strained through various thicknesses of cheesecloth, filtered brilliantly clear, burred with light and heavy pressure on the cone, hand-peeled and pressed juice, and strained burred juice to which was added varying amounts of ground albedo, flavedo, whole peel, and vascular tissue, broken seeds, and whole seeds. The unstrained burred juice or that from which seeds only were removed was too pulpy and deteriorated rapidly in flavor, acquiring a slightly bitter taste after 13 months of storage. Samples of burred juice that were strained too free of pulp or were filtered were flat and lacked orange flavor prior to storage, although they changed less in flavor during storage. The samples to which albedo, flavedo, whole peel, and vascular tissue were added did not keep well in storage, large changes in flavor occurring after 2 months, and they eventually became flat or stale or both with varying degrees of off-flavors, depending upon the amount and kind of material added. Those containing pits, especially broken pits, became extremely bitter. The best juice was that prepared by burring the halved oranges with moderate pressure, followed by straining through a single thickness of cheesecloth.

The undesirable flavors caused were due to the extraction of undesirable principles and perhaps to the catalytic effect of the pulp upon oxidative and other changes. They were perhaps caused in part by the action of oxidizing enzymes since an experiment showed the juices, to which were added peroxidase preparation from the peel, and apple or pear juice, deteriorated more rapidly than the untreated juices.

Effect of Added Acids and Sugars. The effect of acids, sugar, and dilution on the keeping quality of juice from Riverside Valencia oranges was tested. It was found that the addition of sugar, sirup, water, lemon, or grapefruit juice to orange juice for freezing preservation cannot be recommended. However, the addition of about 0.5 per cent citric acid may prove beneficial at times.

Effect of Sulfites. In order to determine the effect of sulfites on the flavor and keeping quality of frozen orange juice, 25, 50, 100, and 500 p. p. m. of sulfurous acid were added as such, and in another series equivalent amounts of potassium metadisulfite were added. It was found that small amounts of sulfur dioxide (25 to 50 p. p. m.) protect against flavor changes in freezing storage. This effect was most pronounced at first but decreased upon longer storage. The greater the concentration of sulfur dioxide the more complete was the preservation of the fresh orange flavor, although concentrations in excess of 50 p. p. m. were found undesirable because the sulfurous acid present was perceptible to the taste.

Effect of Flash Pasteurization. Untreated and deaërated juices were pasteurized at various temperatures and cooled under various conditions. It was found that after prolonged storage deaërated or untreated juices which were rapidly heated to temperatures varying from 165° to 185° F. (73.9° to 85° C.) and rapidly cooled in an ice and salt mixture were of fresher flavor than those which were not flash-pasteurized. Deaëration prior to flash-pasteurization or the temperature to which the juices were heated apparently had but little effect on the keeping quality of the juices. However, the rate of cooling had an important effect, the quicker the heated juice was cooled and the less time it was exposed to high temperatures, the less cooked flavor it had. Pasteurization deepened the yellow and reduced the orange color of the juice. Juice heated to 165° F. was of sweeter flavor than that heated to higher temperatures.

Effect of Precooling the Fruit Prior to Extraction. The use of precooled fruit may increase the absorption of oxygen by the juice during extraction and render the removal of dissolved and absorbed gases more difficult; but on the other hand it decreases the rate of change of flavor during extraction and subsequent handling prior to freezing storage. A number of the previous tests were repeated, using Riverside Valencias stored at 32° F. (0° C.) for about 6 days and cooled to 32° to 35° F. (0° to 1.7° C.).

The fruit was burred at room temperature, but the initial temperature of the juice varied from 47.5° to 49° F. (8.6° to 9.4° C.) and the temperature after deaëration varied from 57.5° to 59.5° F. (14.2° to15. 3° C.). Samples of juice deaërated under 15-, 25-, and 29-inch (38.1-, 63.5-, and 73.7-cm.) vacuums, respectively, and samples of untreated and deaërated juice closed at atmospheric pressure and under a vacuum of 20 inches (50.8 cm.), respectively, were prepared. After 13 months of storage all the samples were of remarkably fresh flavor, considering the long storage period. The deaërated samples still retained their superiority, but the differences between the various members of the series were not very pronounced.

Effect of Storage of Fruit. About three dozen fruit stored at room temperature were removed at intervals of a week or less. Samples stored at 33° F. (83.8° C.) were removed at intervals of 2 weeks. The juice was extracted, frozen, and stored for subsequent examination. The juice expressed on progressive dates from fruit stored at 33° F. showed a loss in flavor during subsequent freezing storage of the juices; this loss increased in extent with increase in the storage period of the fruit. In all cases the juice extracted from the fresh fruit immediately on arrival—i. e., 2 days after picking—was fresher in flavor initially and retained its flavor better during storage. The flavor of frozen juice prepared from fruit stored for 2 weeks at room temperature and then stored for 79, 234, and 411 days after extraction was about equal to that prepared from fruit stored 30 days at 32° F. (0° C.). Both, however, were inferior to the juice from the fresh fruit. As a result of this and other similar experiments, the authors do not recommend storage for longer than one week at room temperature, or about 2 weeks in cold storage.

Samples of juice were extracted from Valencia oranges picked at intervals of 2 weeks at Riverside from August 15 to October 24, 1931, and from April 24 to September 24, 1932. Samples of juice were extracted from Washington navel oranges picked periodically at Oroville from November 10, 1931, to February 25, 1932, and from navels grown at Riverside from November 7, 1931, to April 16, 1932. No definite correlation between composition and keeping quality was found, and to conserve space the analyses of the various lots of juices are not given. On November 16, 1932, when the samples of the first lot of Riverside Valencia series were removed for examination, it was found that untreated juice from fruit picked on August 29, 1931, was of fair to good orange flavor and had more orange flavor and aroma than the other samples; juice from fruit picked on September 12, 1931, was markedly flatter in flavor, and the juices from fruit picked after this date were flat, too sweet, and lacked orange flavor. On April 6, 1932, no change was noted which would indicate that it was desirable to harvest Valencia oranges for freezing preservation later than September 1 under conditions such as existed at Riverside during the 1931 growing season. No bitter taste developed in this series.

Samples of the second series of Riverside Valencia oranges were removed for examination on October 5, 1932. Samples of juice from fruit picked prior to June 4, 1932, were sour, immature, bitter, and lacked orange flavor. Those from fruit picked between June 4 and July 2, 1932, did not develop bitterness but were sour and immature in flavor. The samples extracted from fruit picked from July 2 to 29, 1932, were full flavored and of good aroma, while juice extracted from fruit picked between August 13 and September 24, 1932, were increasingly overmature, flat, and too sweet in taste. The light yellow color of juice from immature fruit changed to a yellowish orange color with increased maturity. Apparently the Valencias picked in Riverside during July 1932, when they were at their optimum as determined by color, flavor, and growing conditions, were superior for juice to fruit picked earlier or later. Observations prior to and subsequent to this test have indicated that, in general, the fruit at its optimum stage of maturity yields a juice of the best flavor and keeping quality.

Juices from Washington navels picked at Oroville during the period from November 10, 1931, to February 25, 1932, were bitter. The fruit picked early in the season yielded a juice that was intensely bitter, sour, and rather stale in flavor, although the degree of bitterness decreased somewhat as the season advanced. There was but little difference in degree of bitterness of the deaërated and untreated samples.

After storage until October 4, 1932, the bitter taste was present in Riverside Washington navels picked during the period November 7, 1931, to April 5, 1932. The color ranged from light yellow to orange. The bitter taste decreased with increase in maturity. The juice from oranges picked at the end of the season, although not bitter, was decidedly lacking in orange flavor and aroma. Apparently both the Oroville and Riverside Washington navels are not as suitable for juice purposes as Valencia oranges when the juice is extracted by burring, because early in the season the burred navel juice turns bitter, and late in the season it lacks flavor.

The bitter taste is not present in the freshly burred juice but develops upon standing if certain tissues of the fruit are present. The rate of development of the bitter taste in burred orange juice upon standing at room temperature decreases with maturity. A bitter taste can be detected in the juice of immature fruit within a half-hour at room temperature, but this "incubation period" increases to several hours as the fruit becomes more mature. In some cases no bitter taste developed in navel juice brilliantly filtered shortly after extraction, but in other cases some bitter taste appeared. The bitter principle was found to be localized primarily in the inner peel and veins and locular wall tissues. This finding confirms the results obtained by Camp et al. (*1*) on this point.

Cruess (*3*) and McNair (*11*) have pointed out that "a bitter taste develops in the untreated juice if it is long exposed to air." The writers have noticed that the bitter taste did not develop as rapidly in deaërated as in the untreated navel juice. However, in a preliminary test, navel orange juice held under vacuum developed a bitter taste although at a somewhat slower rate than when exposed to the air. It is possible that the bitter principle may be present in a complex such as the glucoside-glucose complex postulated by Hall (*5*) for certain glucosides of the navel orange in which form it is not bitter, but that hydrolysis of this complex liberates the bitter principle. Tests are under way to isolate this bitter principle complex and to determine its mode of formation.

From the analyses of the juices it is difficult to determine the range of composition at which the flavor and keeping quality is best.

FREEZING STORAGE OF ORANGES. Since orange juice deteriorates less rapidly in the fruit than when extracted during storage at room temperature and at 32° F. (0° C.), it was thought that it might be possible to preserve whole oranges for subsequent extraction by freezing storage. A box of fruit was allowed to freeze in air at 0° to 10° F. (−17.8° to −12.2° C.) and after 2 months was removed for examination. About half the oranges had burst upon freezing. Upon thawing, the flesh of the fruit was flabby but tough in texture, the peel was markedly limp and somewhat browned and dried. It was easily separated from the pulp. The oranges were markedly stale and somewhat brackish in flavor, and the extracted juice was unpalatable.

ACKNOWLEDGMENT

The authors wish to thank the following persons who coöperated in furnishing the fruit used in these experiments: R. G. La Rue of the Citrus Experiment Station, C. V. Vernon of the San Joaquin Fruit Company, and B. L. Smith of Butte County.

The helium used in the tests was furnished through the kindness of J. T. Howington of the Helium Company of Kentucky.

LITERATURE CITED

(1) Camp, A. F., Traub, H. P., Gaddum, L. W., and Stahl, A. L., Fla. Agr. Expt. Sta., *Bull.* 248, 1–56 (1932).
(2) Chace, E. M., and Poore, H. D., IND. ENG. CHEM., 23, 1109–12 (1931).
(3) Cruess, W. V., Calif. Agr. Expt. Sta., *Bull.* 244, 157–70 (1914).
(4) Gore, H. C., U. S. Dept. Agr., *Bull.* 241, 1–19 (1915).
(5) Hall, J. A., *J. Am. Chem. Soc.*, 47, 1191–5 (1925).
(6) Irish, J. H., Calif. Agr. Expt. Sta., *Circ.* 313, 1–61 (1932).
(7) Joslyn, M. A., *Fruit Products J.*, 9 (11), 13–15 (1930).
(8) Joslyn, M. A., IND. ENG. CHEM., 24, 665–8 (1932).
(9) Matthew, Alexander, M. S., Thesis in Agricultural Technology, Univ. of Calif., 1928.
(10) McDermott, F. A., IND. ENG. CHEM., 8, 136–8 (1916).
(11) McNair, J. B., Field Museum Nat. History, *Botanical Ser.* VI (1), ix + 212 (1926).
(12) Szent-Györgyi, Albert, *Biochem. J.*, 22, 1387–1409 (1928).
(13) Turnbow, G. D., and Cruess, W. V., Calif. Agr. Expt. Sta., *Bull.* 434, 1–38 (1927).

RECEIVED August 8, 1933.

High-Temperature Carbonizing Properties of Coal

Splint and Bright Coal from the Elkhorn Bed in Letcher County, Ky.

A. C. Fieldner, J. D. Davis, D. A. Reynolds, and C. R. Holmes
U. S. Bureau of Mines Experiment Station, Pittsburgh, Pa.

Representative samples of bright and splint coal and a sample containing 40 per cent of splint and 60 per cent of bright coal from the Elkhorn bed are carbonized at 900° C. (1652° F.) in the Bureau of Mines carbonizing apparatus, and the yields of carbonization products determined and compared. The quality of carbonization products is also compared.

The yield of coke from the splint coal is higher than that from bright, and its quality is better. It is more resistant to shatter, and the softening temperature of the ash which it contains is 450° F. higher than that of the ash from the coke of the bright coal.

There is little difference in the yield and quality of gas from the bright and splint coals, that from the bright coal being slightly superior. The bright coal, however, yields appreciably more tar than the splint and its quality is different. It is more phenolic and less benzenoid in character.

The carbonizing properties of a representative sample of Elkhorn coal from Mine 204, Elkhorn bed, Letcher County, Ky., have been determined at carbonizing temperatures, 500° C. (932° F.) to 1100° C. (1980° F.), over 100° intervals, and the results of the work have been published (*1*). In a later investigation (*4*) confined to the petrography of coal from this mine, it was found to contain considerable splint[1] and it was desired to know how the splint content would affect its carbonizing properties—those manifested at high carbonizing temperatures in particular. The present report deals with the carbonizing properties at 900° C. (1652° F.) carbonizing temperature of top-bench coal which contains no splint, bottom-bench coal containing 40 per cent splint, and splint segregated from the bottom-bench coal. For convenience in discussion and brevity in the tables these samples are designated, respectively, as top bench, bottom bench, and splint coal.

SAMPLING

The samples were collected from Mines 204, 205, 206, 207, and 208 at Jenkins in Letcher County, Ky. Twenty large channel samples taken only at points actually producing coal were combined to represent the output of the five mines. The samples representing the bottom bench were kept separate from those of the top bench, measurements of the layers of the bed for each sample being recorded. The amount of splint coal in the bottom bench was calculated from the average thickness of the splint and bright coal layers. A composite sample to represent pure splint was taken at the points where the channel samples were obtained. Bureau of Mines petrographers inspected the samples on arrival at the station and estimated that the top bench was practically free from splint, that the bottom bench contained about 40 per cent splint, and that the splint sample was at least 90 per cent splint. The samples were coarse, having a large proportion of lump of 3-inch size. The column sample of coal from Mine 204 previously examined (*4*) contained 25 per cent semisplint in the top bench and 32 in the bottom. Since the sampler found no splint in the top bench and only 40 per cent splint in the bottom bench, it is evident that he did not recognize the semisplint coal so characterized by Bureau of Mines petrographers, but considered it as bright coal. The samples were tested as segregated by the sampler because of the impracticability of distinguishing and separating semisplint[1] by a macroscopic method. Both the top and bottom benches, therefore, must have contained semisplint. The segregated splint sample, because of its uniformly dull appearance and hardness, can be taken as practically pure splint. Several thin sections from lumps selected at random from the splint sample were made, and the structure of the coal was found to agree very well with that previously found for the splint coal from the column taken from Mine 204.

Table I. Analyses[a] of Samples as Carbonized

Coal	Lab. No.	Condition	Proximate Analysis				Ultimate Analysis					Calorific Value	Softening Temp. of Ash
			Moisture	Volatile matter	Fixed C	Ash	H	C	N	O	S	B. t. u./lb.	° F.
Top-bench bright coal, free from splint	A89178	1	1.8	36.4	60.1	1.7	5.6	82.2	1.6	8.4	0.5	14,630	2300
		2	...	37.0	61.2	1.8	5.5	83.7	1.6	6.9	0.5	14,900	
		3	...	37.7	62.3	...	5.6	85.3	1.6	7.1	0.5	15,160	
Bottom-bench bright coal containing 40% splint	A89179	1	1.5	35.6	59.8	3.1	5.4	81.0	1.5	8.4	0.6	14,410	2760
		2	...	36.1	60.7	3.2	5.3	82.2	1.5	7.2	0.6	14,630	
		3	...	37.3	62.7	...	5.5	84.9	1.6	7.4	0.6	15,110	
Splint from bottom bench	A89031	1	1.4	35.3	59.6	3.7	5.3	81.2	1.4	7.9	0.5	14,450	2800
		2	...	35.8	60.4	3.8	5.2	82.3	1.5	6.7	0.5	14,650	
		3	...	37.2	62.8	...	5.4	85.5	1.5	7.1	0.5	15,220	

[a] 1, sample as received; 2, dried at 105° C.; 3, moisture- and ash-free.

---

[1] The term "splint" is synonomous with "durain" of the English, and *Mattkohle* of the German nomenclature. Macroscopically it is lusterless as compared with the rest of the coal to which the term "bright coal" is ordinarily applied. Under the microscope, splint in thin sections is distinguished by predominance of opaque bodies of undetermined composition and the prevalence of a characteristic megaspore. Semisplint has the same microscopic appearance except that it contains less opaque matter. Macroscopically it has some luster and is not readily distinguished from bright coal.

Analyses of Samples

Table I gives the proximate and ultimate analyses of the samples as carbonized, and Table II the sieve analyses of the samples as prepared for carbonization.

Table II. Sieve Analyses of Samples as Carbonized

Mesh	Sample A89178	Sample A89179	Sample A89031
	%	%	%
On 4	3.0	4.5	12.3
Through 4 on 8	28.4	39.9	48.7
Through 8 on 14	26.4	24.0	20.0
Through 14 on 35	25.1	20.3	12.8
Through 35 on 80	9.6	6.9	3.8
Through 80 on 150	3.2	2.2	1.2
Through 150 on 200	1.2	0.7	0.4
Through 200	3.1	1.5	0.8

The splint coal is of no different rank from the bright coal as judged from its volatile matter content. In previous work on splint and bright coals it has been found that the volatile matter content of the splint may run higher or lower than that of the bright coal (*2*) from the same bed, depending on its spore content; that is, the richer the splint is in spores, the higher its volatile matter content. The splint from this bed is moderately rich in spores. The ash content of the splint coal and that from the bottom bench is practically twice as high as that from the bright coal, but it is much more refractory. The softening temperature reached 1540° C. (2800° F.) as compared with 1260° C. (2300° F.) for the bright coal. The sieve analyses show the splint coal to be much more resistant to crushing than the bright coal, as would be expected.

Results of Carbonization Tests

Carbonization tests were made in the 13-inch (33-cm.) retort (41 to 45 kg. or 90 to 100 pounds capacity) in duplicate at 900° C. (1652° F.) carbonizing temperature, and the yields and quality of the carbonization products were determined. Tables III to XII, inclusive, give the results obtained.

Yields of Carbonization Products

Table III gives the yields of carbonization products obtained. The bright coal gives a lower yield of coke and higher yields of tar and gas than either the splint or bottom-bench coal, although the differences in yields are not great except for the tar. But some of the differences are due to differences in ash and moisture content and are not chargeable to variations in the coal substance. For example, if the heating value in gas per pound of coal carbonized (Table VII) is calculated to the ash- and moisture-free basis, one obtains: for splint coal 3392, for bottom bench 3334, and for top bench 3487 B. t. u. per pound of coal substance (4155, 4084, and 4272 cal., respectively, per kg. of coal). Thus the yield of B. t. u. of gas from the bottom bench on this basis is 4.4 per cent lower than that of the bright coal comprising the top bench, and the difference between the pure splint and the bright coal is 2.7 per cent. The yields of tar on the moisture- and ash-free basis are 67, 64, and 57 liters (17.7, 17.0, and 15.0 gallons) per ton of 2000 pounds for the bright coal, bottom bench, and splint, respectively. Thus the bright coal substance yields 15 per cent more tar than the splint—a significant difference. Furthermore, there are significant differences in the quality of these tars, as will be shown later. On calculating the yield of tar from the proportions of splint and bright coal in the bottom bench, one obtains:

$$
\begin{aligned}
15.0 \times 0.359 &= 5.40 \text{ gallons}\\
17.7 \times 0.641 &= 11.34 \text{ gallons}\\
\text{Total } &\overline{16.74} \text{ gallons (63.4 liters)}
\end{aligned}
$$

This figure of 16.7 is in fair agreement with the figure 17.0 found by carbonization.

Quality of Cokes

Table IV gives the analyses of the cokes obtained, and Table V shows their physical properties. The bright coal or top bench is a little lower in volatile matter content than the other two cokes, and the softening temperature of the ash, as one would expect from similar determinations on the coal samples, is low. Otherwise there are no significant differences in the coke analyses. However, there are considerable differences in their physical properties. The top-bench bright coal produces a light porous coke of low resistance to shatter and breakage as compared with that from the selected splint and the bottom-bench coal containing 40 per cent splint. Furthermore, there is a gradation in resistance of the cokes. The coke from the selected splint coal is much the strongest by this measure, the coke from the 40 per cent splint mixture comes next in order, and the coke from the bright coal is weakest. This splint coal con-

Table III. Yields of Carbonization Products of Bright and Splint Coal, as Carbonized at 900° C. (1652° F.)

Coal	Yields, Per Cent by Weight of Coal: Coke[b]	Gas[c]	Tar[b]	Light oil	Ammonia	Liquor	Total	Yields per Ton[a] of Coal: Gas[c]	Tar	Light oil	$(NH_4)_2SO$
								Cu. ft.	*Gal.*[d]	*Gal.*[d]	*Lb.*
Splint	68.6	15.8	7.0	0.93	0.15	6.2	98.7	10,600	14.5	2.6	21.6
Bottom-bench	68.4	15.9	7.7	1.14	0.16	6.8	100.1	10,300	16.2	3.2	24.2
Top-bench	66.9	16.3	7.9	0.92	0.17	6.7	98.9	10,700	16.8	2.6	22.4

[a] 2000 pounds.
[b] Dry.
[c] Stripped of light oil, saturated at 60° F. and 30 inches of mercury.
[d] U. S. gallon, or 3.785 liters.

Table IV. Analyses of Coke, Dry Basis

Coal	Proximate Analysis: Volatile matter	Fixed carbon	Ash	Ultimate Analysis: H	C	N	O	S	Calorific Value	Softening Temp. of Ash
	%	%							*B. t. u./lb.*	*° F.*
Splint	1.5	92.8	5.7	0.8	91.1	1.4	0.6	0.4	13,700	2720
Bottom-bench	1.5	93.4	5.1	0.8	91.6	1.4	0.6	0.5	13,820	2680
Top-bench	1.0	96.1	2.9	0.7	94.0	1.5	0.5	0.4	14,140	2270

Table V. Physical Properties of Coke (as Received)

Coal	Specific Gravity: True	Apparent	Cells	Shatter Test, Cumulative Per Cent on: 2-in. sieve[a]	1.5-in. sieve	1-in. sieve	0.25-in. sieve	Tumbler Test, Cumulative Per Cent on: 2-in. sieve	1.5-in. sieve	1-in. sieve	0.25-in. sieve
			%								
Splint	1.84	0.84	54.2	34.5	70.0	92.8	98.6	0.9	11.5	58.2	74.8
Bottom-bench	1.85	0.84	54.6	16.6	51.2	86.5	98.3	0	4.4	49.5	77.7
Top-bench	1.84	0.79	57.1	7.0	34.6	79.0	98.1	0	0.5	39.7	78.6

[a] Standard sieves, actual dimensions of square openings

tains some translucent attritus (approximately 25 per cent) (*4*) which may impart the degree of fusibility requisite for the production of a good coke. The bright coal probably is much too fusible and therefore it produces a light porous coke.

TABLE VI. SCREEN ANALYSIS OF COKE

COAL	CUMULATIVE PER CENT ON: 4-in. screen[a]	3-in. screen	2-in. screen	1.5-in. screen	1-in. screen
Splint	0	18.2	59.5	86.4	97.0
Bottom-bench	0	15.3	53.4	82.9	94.2
Top-bench	1.5	22.1	56.4	81.0	94.3

[a] Standard sieves, actual dimensions of square openings.

TABLE VII. PHYSICAL AND CHEMICAL PROPERTIES OF GAS

COAL	SP. GR.	GROSS HEATING VALUE[a] PER CUBIC FOOT Detd.	Calcd.	PER POUND OF COAL	H_2S PER 100 CU. FT.	COMPOSITION, DRY, PER CENT BY VOLUME: CO_2	Illuminants	O_2	H_2	CO	CH_4	C_2H_6	N_2
		B. t. u.	*B. t. u.*	*B. t. u.*	*Grains*								
Splint	0.395	605	600	3210	150	1.7	5.6	0.2	53.1	7.3	30.5	1.0	0.6
Bottom-bench	0.409	616	605	3170	210	1.6	5.3	0.4	52.3	7.2	30.2	1.9	1.1
Top-bench	0.406	618	609	3300	170	1.6	5.5	0.2	52.0	7.6	29.8	2.2	1.1

[a] Stripped of light oil, saturated at 60° F. and 30 inches of mercury.

TABLE VIII. ANALYSIS OF DRY TAR

COAL	SP. GR.[a]	HEATING VALUE	ULTIMATE ANALYSIS H	C	N	O	S	FREE CARBON	ANTHRACENE SALTS	NAPHTHALENE SALTS	BOILING RANGE AT: 0–170° C. (32–338° F.)	170–235° C. (338–455° F.)	235–270° C. (455–518° F.)	270–350° C. (518–662° F.)	RESIDUE
		B. t. u./lb.	*Per cent by weight*												
Splint	1.16	16,410	5.9	90.2	1.0	2.5	0.4	6.29	2.23	4.27	6.3	16.6	6.2	14.7	56.2
Bottom-bench	1.14	16,370	6.3	88.6	1.0	3.7	0.4	5.19	1.63	1.05	6.5	20.3	6.3	16.3	50.6
Top-bench	1.13	16,410	6.4	88.0	1.0	4.3	0.3	5.65	1.24	0.39	5.3	20.3	7.2	16.5	50.7

[a] At 15.6°/15.6° C. (60°/60° F.).

TABLE IX. ANALYSES OF TAR DISTILLATE AND LIGHT OIL

COAL	DISTILLATE, PER CENT BY VOL. OF DRY TAR Acids	Bases	Neutral oils	NEUTRAL TAR OIL Olefins	Aromatics	Paraffins and naphthenes	REFINED LIGHT OIL FROM GAS Benzene	Toluene	Paraffins	Solvent naphtha	CRUDE LIGHT OIL FROM GAS Olefins	Naphthalene
					% by volume			*% by volume*			*% by vol.*	*% by wt.*
Splint	4.7	1.9	30.6	12.3	83.8	3.9	68.3	21.4	4.6	5.7	10.0	0.16
Bottom-bench	8.8	2.3	35.7	11.3	80.1	8.6	57.1	21.5	10.0	11.4	14.7	0.14
Top-bench	10.2	1.9	35.6	10.7	79.4	9.9	57.4	21.2	10.1	11.3	13.0	0.19

TABLE X. TAR AND TAR CONSTITUENTS

(In gallons[a] per ton)

COAL	TOTAL TAR	ACIDS	BASES	NEUTRAL OILS	OLEFINS	AROMATICS	PARAFFINS AND NAPHTHENES	PITCH
Splint	14.5	0.68	0.27	4.44	0.55	3.72	0.17	8.15
Bottom-bench	16.2	1.43	0.37	5.78	0.65	4.63	0.50	8.20
Top-bench	16.8	1.71	0.32	5.98	0.64	4.75	0.59	8.52

[a] U. S. gallon (3.785 liters) per ton of 2000 pounds.

TABLE XI. LIGHT OIL AND LIGHT OIL CONSTITUENTS

(In gallons per ton)

COAL	CRUDE LIGHT OIL	OLEFINS	BENZENE	TOLUENE	PARAFFINS	SOLVENT NAPHTHA
Splint	2.58	0.26	1.58	0.50	0.11	0.13
Bottom-bench	3.21	0.47	1.57	0.59	0.27	0.31
Top-bench	2.60	0.34	1.30	0.48	0.23	0.25

QUALITY OF GASES

The bright coal from the top bench gives somewhat the best gas (Table VII), although as previously shown the variation in quality between the samples is only of the order of 4.4 per cent.

QUALITY OF TARS AND LIGHT OILS

Tables VIII to XII, inclusive, give the physical and chemical properties of the tars and light oils. The tar from the splint coal is appreciably different in quality from those of the top and bottom benches (Tables VIII and IX). The main points of difference are: (1) The tar from the splint coal contains less tar acids and paraffins, and more benzenoid hydrocarbons, pitch, free carbon, and naphthalene and anthracene salts than the other tars, these constituents varying with the splint content of the coal. (2) On the basis of quantities of constituents recovered per ton of coal carbonized (Table X) the splint coal contains less tar acids and paraffins than the other two, but the relationship of benzenoid hydrocarbons is reversed. The order of total pitch recovered is also reversed.

TABLE XII. TOTAL LIGHT OIL TO 338° F. (170° C.) and 392° F. (200° C.)

(In gallons per ton)

COAL	LIGHT OIL IN GAS (1)	TAR TO: 338° F. (2)	392° F. (3)	TOTAL LIGHT OIL TO: 338° F. (1) + (2)	392° F. (1) + (3)
Splint	2.58	0.91	1.52	3.49	4.10
Bottom-bench	3.21	1.05	2.15	4.26	5.36
Top-bench	2.60	0.89	2.07	3.49	4.67

These points of difference are sufficient to show that there is an appreciable variation in quality of tar recovered from different types of coal from the same bed. It has also been shown that there is an appreciable difference in the quantity of tar recovered. A higher proportion of tar acids is to be expected from the humic bright coal than from the splint, on the basis of the work of Holroyd and Wheeler (*3*), who have shown recently that durain (probably equivalent to splint coal) yields less of the phenolic oils than vitrain (equivalent to the anthraxylon of American bright coal), and that the tars from the former are the more benzenoid in character.

CONCLUSIONS

1. The bright coal gave a slightly lower yield of coke than the other two samples which contained splint coal, but the quality of the cokes from the splint-containing coals was decidedly superior as judged by results of shatter and tumbler tests.
2. There was little difference in the yield and quality of gas from bright and splint coal.
3. The top-bench, bright coal yielded more tar than the coals containing splint and its quality was decidedly different. It was more phenolic and less benzenoid in character.

4. These variations in carbonizing properties were not characterized by corresponding variations in the volatile matter content of the samples, as has been the case with some coals previously examined; the volatile matter content of the two types of coal and of the mixture is nearly the same.

5. The bright coal alone apparently is too fusible to yield coke of the best quality; the splint coal, ordinarily deficient in fusing properties, has in this coal sufficient translucent attritus to impart the optimum fusing properties for the bed and hence it produces a better coke than the other two samples.

Acknowledgment

The coal samples were collected by C. H. Forester, preparation manager of the Consolidation Coal Company. The analyses of the coal samples shown in Table I were made by H. M. Cooper of the Coal Analysis Section of this station. Analyses of the tar distillate and light oil given in Table IX were made by L. P. Rockenbach of this station.

Literature Cited

(1) Fieldner, A. C., Davis, J. D., and Reynolds, D. A., Ind. Eng. Chem., 22, 1113–23 (1930).
(2) Fieldner, A. C., Davis, J. D., Thiessen, R., Kester, E. B., Selvig, W. A., Reynolds, D. A., Jung, F. W., and Sprunk, G. C., Bur. Mines, *Tech. Paper* 542 (1932).
(3) Holroyd, R., and Wheeler, R. V., *Fuel*, 9, 104–13 (1930).
(4) Thiessen, Reinhardt, Sprunk, G. C., and O'Donnell, H. J., Bur. Mines, *Tech. Paper* 506 (1931).

Received August 26, 1933. Presented before the Division of Gas and Fuel Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

Thermal Properties of Rubber Compounds

I. Thermal Conductivity of Rubber and Rubber Compounding Materials

C. E. Barnett, The New Jersey Zinc Company, Palmerton, Pa.

An apparatus is described for measuring the thermal conductivity of rubber and rubber compounding materials using electric current as the source of heat.

In the majority of cases the thermal conductivities check those found by Williams, using steam as the source of heat. As reported by Williams, no difference is found between smoked sheet and pale crepe rubber, and the state of cure of a compound has no effect on its heat conductivity.

Variations in particle size within the pigment range have no bearing on the heat conductivity of zinc oxide, but extremely coarse oxides have higher conductivities. Chemical constituents, such as are present in slow curing zinc oxides, have no measurable effect on thermal conductivity.

Particle shape has considerable effect on thermal conductivity. Acicular pigments show higher conductivities when the calender grain is parallel to the direction of heat flow rather than across it.

Fast curing carbon black has the same heat conductivity as the slow curing variety; lampblack and graphite show increased thermal conductivities.

The results of this work check those of Williams who showed that thermal conductivity is a straight-line function of the volume per cent of pigment and of rubber.

The purpose of this series of papers is to present and analyze the experimental data on the thermal behavior of rubber compounds which have been obtained during the past few years in the writer's laboratory. Because of the complex nature of the problem, it is impossible to say exactly what a given test measures, much less to correlate the data of the various experiments and to predict results in other tests and in performance. In general, the factors recognized in this laboratory as variables controlling the thermal behavior of a rubber compound are: (1) heat conductivity, (2) heat resistance, and (3) heat generation.

Heat conductivity is recognized as of great importance in vulcanization, in determining the running temperature of rubber tires, and, in general, wherever fairly large masses of rubber are subjected to repeated distortion. With relatively small test pieces, this factor does not have as great a bearing on the results as it does with larger masses of rubber, an important consideration in interpreting laboratory results in terms of performance.

For the purpose of this investigation, heat resistance is considered as a measure of the ability of a rubber compound to withstand high temperatures without undergoing reversion or serious deformation under load. Thermal resistivity is frequently used to mean the reciprocal of thermal conductivity or the resistance which a substance offers to the conduction of heat.

The third factor, heat generation, is of importance in all kinds of tests involving thermal problems. This is probably the most difficult of the three factors to examine in a performance test because of the difficulty of eliminating such variables as thermal conductance and resistance. It is generally accepted that the area of the hysteresis loop formed when rubber is put through a cycle of extension and retraction gives an indication of heat generation. The work of Cotton (*4*) indicates that the area of this loop varies directly with the entire area under the extension curve, but this conclusion may apply only to one particular set of experimental conditions.

From the above discussion it follows that, so far as heat effects are concerned, the most satisfactory rubber compound would be one of high thermal conductivity and resistance and with low heat generation. Future papers are planned to discuss heat resistance and generation. The purpose of the present paper is to consider the first factor studied—heat conductivity.

The first practical work on the subject of the heat conductivity of rubber was that of Somerville (*7*), and adequate data enabling the calculation of the thermal conductivity and diffusivity of compounds were determined by Williams (*8*). For the present investigation, however, more detailed information was required on the effect of the variations obtainable in zinc oxide, covering a range of particle size and chemical analysis.

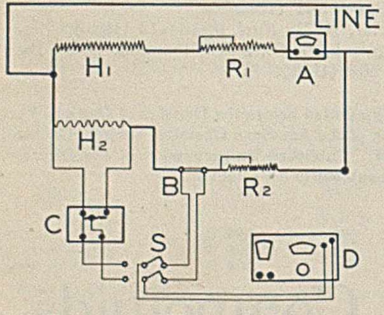


FIGURE 1. HEATING CIRCUIT

Williams determined heat conductivity by covering a closed cylindrical vessel with the material to be studied and measuring the water which collected when steam was passed through the vessel, the outside temperature being controlled by immersion in a constant-temperature bath. It was felt that the substitution of electric current as a source of heat might result in an apparatus which would be more conveniently operated than one using steam and, at the same time, would offer a check on published data by an independent method.

APPARATUS AND PROCEDURE

Figures 1 to 3 are wiring diagrams for the apparatus.

In Figure 1 the heating circuit is shown. H_1 is a compensating heater which surrounds H_2, the calorimeter heater, to prevent lateral flow of heat. R_1 and R_2 are variable resistances controlling the heaters. *A* is an ammeter for measuring the current in the compensating heater. *B* is a shunt, *C* a potential divider, *S* a double-throw switch, and *D* a potentiometer for measurement of electrical energy entering the calorimeter heaters. In the case of alternating current, *B*, *C*, and *D* may be replaced by an a. c. wattmeter, but, since such an instrument of sufficient accuracy was not available, it was necessary to use direct current and the rather complicated auxiliary circuit described above.

Figure 2 shows the calorimeter and the location of the thermocouples. Plates 2 and 3 are heated with two circular elements in each plate, one inside the other. The outer element is used as a guard ring permitting the adjustment of the temperature so that there is no lateral heat flow, and only the area covered by the inner heater is used in the calculation of thermal conductivity. There are thirteen thermocouples on each of these two plates, one in the center and four in each of three circles radiating outward. The outer thermocouples (2*B* and 3*B*) are not read in determining heat conductivity but are used to measure the temperature differential between the compensating and the calorimeter heaters. The remaining thermocouples are connected with the selective switch, S_1, shown in Figure 3, which in turn is connected to a potentiometer and sensitive galvanometer provided for recording the average temperature of that portion of the plate covered by the inner heater. It has been mentioned that the outer thermocouples (2*B* and 3*B*) on the hot plates are used in determining the temperature differential between the two heating elements. This is done by connecting these couples with those from the outer edge of the calorimeter heaters (2*C* and 3*C*) by means of the double pole–double throw switch, S_2, so that an opposing electromotive force is set up between 2*B* and 2*C*. Then, if these temperatures are not equal, a deflection will be shown on the sensitive galvanometer, G_2, when the switch is thrown connecting these couples. With this arrangement it is possible to control the temperature differential between the calorimeter and guard ring within 0.03° C.

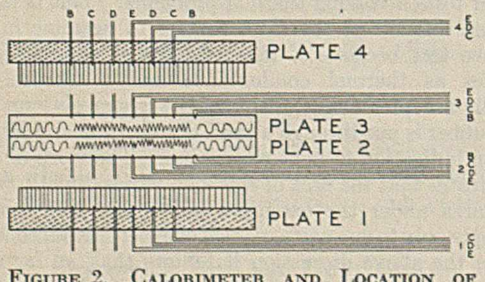


FIGURE 2. CALORIMETER AND LOCATION OF THERMOCOUPLES

The elimination of lateral heat flow is the most important factor in determining the accuracy of the apparatus. It was found that a groove cut almost through the hot plates between the calorimeter and guard ring and packed with insulating material was effective in decreasing this error. Even before this refinement was made, if the differential was as much as 0.3° C., the average error would still be within 5 per cent.

Plates 1 and 4 are equipped with thermocouples in exactly the same manner as described for the hot plates 2 and 3. This permits the measurement of the temperature gradient through the rubber and from this the calculation of the conductivity constant.

Several experiments were made to determine possible sources of error and the extent of their elimination in the apparatus used. Previous workers (*1*) have commented on the effect of air films between the sample and metal plates on the conductivity constant. The error caused by such an air film would decrease as the thickness of the test specimen was increased, but experiments illustrated in Figure 4 show that with the present apparatus the thickness of the test piece could be varied from 0.4 to 2.0 cm. without affecting the conductivity constant.

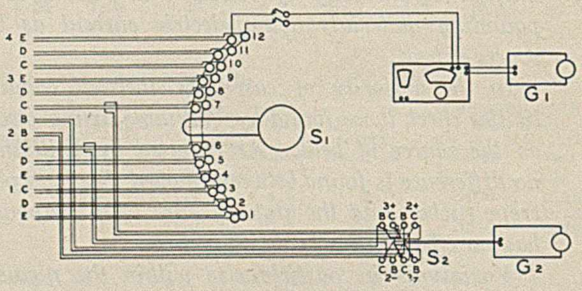


FIGURE 3. CONNECTIONS WITH SELECTIVE SWITCH

In order to check the apparatus in general, as well as the effect of air films, an experiment was designed which would be entirely independent. A small spherical heater was cured into the center of a sphere of rubber 4 inches (10.2 cm.) in diameter. The location of this heater and of the two series of thermocouples for measurement of the temperature gradient is shown in Figure 5. The conductivity constant for a ten-volume zinc oxide compound as measured in this experiment checked results obtained with the flat plate tester almost exactly.

CALCULATION OF WORKING FORMULA

The electric current has been used widely as a source of heat in determining the conductivity of metals and in a few cases for insulating materials (*5*, *6*). In the case of good conductors a long rod of the material can be wrapped in an insulator and the factor of lateral flow of heat neglected. To apply this method to the present problem, the rod is compressed to a flat disk and the following conditions apply: Let two sides of the rubber disk of thickness 1 be kept at constant temperatures, T_1 and T_2, T_1 being larger than T_2. Heat flows through the sample from the higher to the lower temperature. The quantity of heat, *H*, passing through any area, *A*, is proportional to this area, to the temperature gradient, and to the time, *t*, during which the heat flows. Thus we obtain:

$$H = KA\,\frac{(T_1 - T_2)t}{1}$$

where K = a proportionality factor depending upon plate material. K is numerically equal to the heat transferred in unit time through unit area of a plate of unit thickness, if unit difference of temperature is maintained between its two faces. H is equal to the product of the number of watts, EI, applied to the heating elements and the number of calories which are equivalent to one watt second or 0.2389. The working formula thus becomes:

$$K = \frac{0.2389EI \times 1}{A(T_1 - T_2)}$$

Results

Williams has shown that the conductivity of a rubber compound is the sum of the conductivities of its ingredients, each multiplied by its volume per cent in the compound. This means that the curve of volume per cent pigment plotted against heat conductivity is a straight line between the conductivity of rubber and the value for the pigment used. Figure 6 shows these curves for several zinc oxides. In Tables I and II the values for the conductivity of the different pigments were obtained by extrapolation of curves similar to those in Figure 6.

Zinc oxides A, B, and D in Table I are fast-curing oxides with particle sizes of 0.10, 0.40, and 0.20 micron, respectively; F is the same type of oxide but is above the pigment range in particle size. It is apparent that particle size, within the pigment range, has no effect on thermal conductivity but that very coarse oxides have high conductivities. Zinc oxide E is similar to D but is surface-treated for improved mixing properties; this has no effect on its thermal conductivity. The remaining oxides in Table I are of the slow curing variety with particle sizes between 0.30 and 0.40 micron except for the last one which is composed almost entirely of acicular particles. The results show that the slow curing oxides have considerably higher conductivities than fast curing oxides of corresponding particle size. This leaves chemical composition and particle shape as the differences in these two types of zinc oxide which could account for the differences in conductivity. It is possible experimentally to make a fast curing oxide slow and a slow curing oxide fast without changing particle size or shape. This has been done in the case of zinc oxides G and H, and no change in thermal conductivity has resulted. There remains particle shape as the chief variable affecting thermal conductivity, but the experiments on samples I and J show that the calender grain is a large factor in determining the conductivity of materials of irregular particle shape. Sample J which is an acicular oxide shows the same conductivity as the fast curing oxides when the direction of heat flow is across the calender grain but has the second highest conductance when the direction of heat flow is parallel to the calender grain. Zinc oxide I, which is representative of the slow curing oxides available commercially, also shows a variation in conductance depending on the calender grain although the difference is not so great as for the acicular oxide. In both cases sample I has the higher conductivity, the difference being small when the direction of heat flow is parallel to the calender grain.

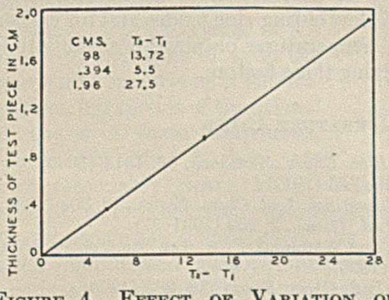


FIGURE 4. EFFECT OF VARIATION OF THICKNESS OF TEST PIECE ON CONDUCTIVITY CONSTANT

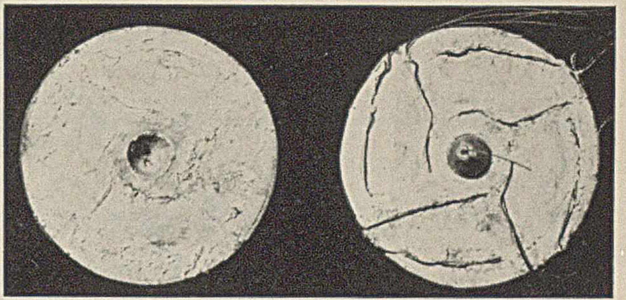


FIGURE 5. LOCATION OF HEATER AND THERMOCOUPLE SERIES IN RUBBER SPHERE

TABLE I. THERMAL CONDUCTIVITY OF ZINC OXIDES

ZINC OXIDE	VOLUME OF PIGMENT	VOLUME % OF PIGMENT	CONDUCTIVITY OF COMPOUND	CONDUCTIVITY CALCD. FOR 100% PIGMENT
			Calorie	*Calorie*
A. Fast curing; particle size 0.10μ	10	8.8	0.000435	0.00165
	30	22.8	0.000643	0.00174
	45	30.6	0.000721	0.00164
	60	37.0	0.000780	0.00162
	70	40.3	0.000871	0.00169
B. Fast curing; particle size 0.40μ	10	8.8	0.000430	0.00160
	30	22.8	0.000632	0.00168
	45	30.6	0.000730	0.00166
	60	37.0	0.000817	0.00167
	70	40.3	0.000869	0.00169
C. Slow curing; particle size 0.35μ	10	8.8	0.000470	0.00200
	30	22.8	0.000723	0.00209
	45	30.6	0.000848	0.00204
	60	37.0	0.000958	0.00205
	70	40.3	0.001070	0.00218
D. Fast curing; particle size 0.20μ	30	22.8	0.000625	0.00167
E. Fast curing; particle size 0.20μ; surface-treated with fatty acid	30	22.8	0.000620	0.00163
F. Fast curing; extremely coarse	30	22.8	0.000740	0.00216
G. Slow curing; particle size 0.35μ; original	30	22.8	0.000689	0.00193
H. Same as G but fast curing	30	22.8	0.000686	0.00192
I. Slow curing; particle size 0.35μ; calender grain normal to direction of heat flow	30	22.8	0.000733	0.00212
I. Same as above but calender grain parallel to direction of heat flow	30	22.8	0.000802	0.00243
J. Slow curing; acicular; calender grain normal to direction of heat flow	20	16.4	0.000537	0.00164
J. Same as above but calender grain parallel to direction of heat flow	20	16.4	0.000640	0.00225

TABLE II. THERMAL CONDUCTIVITY OF RUBBER COMPOUNDS

PIGMENT	THERMAL CONDUCTIVITY		
	Williams (*8*)	N. J. Zinc Co.	
Zinc oxide, fast curing	0.00166	0.00166	0.00167
Iron oxide	0.00132	0.00129	0.00134
Dixie clay	0.00058	0.00105	0.00107
Lithopone	0.00094	0.00092	0.00092
Blanc fixe	0.00078	0.00078	0.00079
Zinc sulfide		0.00108	0.00110
Whiting	0.00084	0.00083	0.00085
Talc	0.00058	0.00089	0.00090
Asbestine		0.00097	0.00098
Magnesium carbonate	0.00103	0.00057	0.00057
Antimony sulfide	0.00021[a]	0.00027[b]	0.00027[b]
Carbon black (slow curing)	0.00067	0.00068	0.00064
Carbon black (fast curing)	.....	0.00067	0.00068
Lampblack	.....	0.00138	0.00142
Graphite (Acheson)	.....	0.00217	0.00217
Diphenylguanidine	.....	0.00034	
Mercaptobenzothiazole	.....	0.00045	
Sulfur	0.00012	0.000296	0.000300

[a] 12 per cent sulfur.
[b] 0.9 per cent sulfur.

Table II shows the results obtained for rubber and several compounding ingredients. The figures given are not equivalent to the conductivity which the pigments would show as powders in air but are suitable for use in the calculation of the thermal conductivities of rubber compounds. Brown and Furnas (*3*) have measured the thermal conductivity of pow-

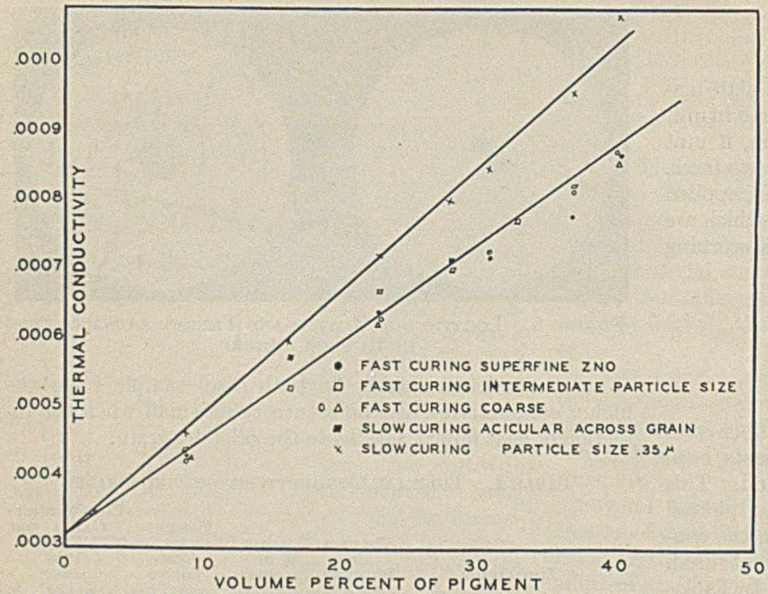


FIGURE 6. HEAT CONDUCTIVITY VS. VOLUME PER CENT PIGMENT FOR SEVERAL ZINC OXIDES

dered ferric oxide and report values varying from 0.00092 calorie at 125° C. to 0.00133 at 700°, while Bidwell (*2*) working with a rod of fused iron oxide reported conductivities ranging from 0.00130 calorie at 160° C. to 0.00255 at 700°; the value obtained in the present investigation was 0.00132 calorie.

As stated by Williams, no difference was found for smoked sheet, pale crepe, cured or uncured rubber. The values for zinc oxide, carbon black, iron oxide, lithopone, blanc fixe, and whiting checked closely. The conductivities obtained for antimony sulfide, sulfur, and talc are somewhat higher than the recorded values, while the values for clay and magnesium carbonate are almost exactly reversed. In this investigation three clays of varying properties were tested, but all were within a few points of the value given above for Dixie clay. No difference was found in the conductivities of fast and slow curing carbon blacks, but lampblack had an increased conductivity while graphite was still higher.

IMPORTANCE OF THERMAL CONDUCTIVITY DATA

In order to discuss the significance of the data on thermal conductivity and its importance in the broader problem of the thermal properties of rubber, it is necessary to make assumptions regarding the heat generation of a rubber compound under some particular set of conditions.

For instance, the equilibrium temperature at the center of a sphere when heat is generated at a constant rate throughout the sphere may be expressed by the equation:

$$T \text{ center} = \frac{cr^2}{6K} + Ts$$

where c = rate at which heat is generated
r = radius of sphere
K = thermal conductivity of compound
Ts = outside temperature

Compounds of the type of A and B below have been used for a number of thermal tests in the writer's laboratory:

	A	B	C
Rubber	500	500	500
Slow curing zinc oxide	750	...	50
Fast curing zinc oxide	...	750	...
Sulfur	20	20	20
Carbon black	45	45	263
Diphenylguanidine	10	10	10

K for compound A is 0.00065, for B, 0.00058; if most of the zinc oxide is replaced by an equal volume of carbon black as in C, *K* becomes 0.000405. If the time is taken in minutes, these values must be multiplied by 60.

If it is assumed that heat is generated throughout the sphere at the rate of one calorie per minute, that the radius of the sphere is 5 cm. and the outside temperature 67° C., the equilibrium temperatures at the centers of the above compounds are 175° C. for A, 187° for B, and 235° for C. The figure given above for the rate of heat generation was derived from the time-temperature curve in a test using the high-zinc compound, A. If the early part of this curve is taken, the temperature difference between the inside and outside of the rubber is small, and consequently the amount of heat conducted away is also small. Knowing the specific gravity and specific heat of the compound, the rate of heat generation necessary to produce the rise in temperature obtained may be readily calculated. The largest error in the above calculation must be that of assuming the same heat generation for fast and slow curing zinc oxides and for carbon black, but at least the temperatures obtained are compatible with experiments involving these factors.

LITERATURE CITED

(1) Anonymous, *J. Inst. Elec. Engrs.* (London), 68, 1313 (1930).
(2) Bidwell, *Phys. Rev.*, 10, 756 (1917).
(3) Brown and Furnas, *Trans. Am. Inst. Chem. Engrs.*, 18, 309 (1926).
(4) Cotton, *Inst. Rubber Ind. Trans.*, 7, 209 (1931–32).
(5) Hartman, Westmont, and Wienland, *Proc. Am. Soc. Testing Materials*, 28, Pt. 2, 820 (1928).
(6) Heilman, *Trans. Am. Inst. Chem. Engrs.*, 18, 283 (1926).
(7) Somerville, *Rubber Age* (N. Y.), 9, 131 (1921).
(8) Williams, IND. ENG. CHEM., 15, 154 (1923).

RECEIVED September 20, 1933. Presented before the Division of Rubber Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.

EXPLOITATION OF ITALY'S OIL RESOURCES PLANNED. Intensive exploitation of Italy's oil resources is planned for the next five years, according to a report from the American consulate, Genoa. All activities in connection with petroleum production and distribution, the report shows, are carried on by the Azienda Generale Italiana Petroli, 60 per cent of whose stock was owned originally by the Italian Government.

During the three years ended June 1933, this corporation was granted an annual government subsidy of 6,000,000 lire to carry on its researches. In August the government authorized it to continue exploring and drilling activities for a period of five years and appropriated for this purpose a total of 90 million lire.

According to a recent report of the A. G. I. P., development of Italy's petroleum resources has thus far been encouraging. The company has not only perfected and consolidated its technical organization for executing the vast and difficult task, but it has made detailed studies in all sections of Italy where oil-bearing beds would be likely to exist.

From the commencement of its explorations until June 30, 1933, the A. G. I. P. had perforated one hundred twelve wells, of which fifty-nine have been abandoned. Thirty-seven wells are being worked, and sixteen are either in process of being installed with equipment or are being sunk to further depths. During the fiscal year 1932–33 the output of petroleum amounted to 2722 metric tons, compared with 2310 tons in the preceding fiscal period.

The A. G. I. P. plans to extend its fields of explorations, hitherto confined almost entirely to the foothills of Emilia, to a good part of the Padana Valley, the Apennine-Adriatic Coast, and to vast sections of south Italy and Sicily. It is calculated that a total of ninety borings will be made, some of very great depths.

Symposium on Hydrocarbon Decomposition

Presented before the Division of Petroleum Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.

Thermal Treatment of Gaseous Hydrocarbons

I. Laboratory Scale Operation

A. E. Dunstan, E. N. Hague, and R. V. Wheeler

Anglo-Persian Oil Company, Ltd., London, England

A review is presented of the mechanisms of thermal decomposition and polymerization of the gaseous hydrocarbons. Conversions to motor benzene, distilling below 200° C., of 16 to 25 per cent with paraffins (methane excepted) and 25 to 30 per cent with olefins are readily obtained by atmospheric pressure treatment at 750° to 950° C. The gasoline fraction contains benzene, toluene, styrene, m- and p-xylenes, and indene, while the higher boiling products contain naphthalene, anthracene, phenanthrene, and chrysene. By the polymerization of olefins at pressures between 200 and 2000 pounds per square inch (14.05 to 140.5 kg. per sq. cm.) and temperatures 300° to 550° C. conversions into liquids up to 92 per cent are attained. Of the liquid hydrocarbons obtained, 86 per cent is in the gasoline range and has about five-sixths the blending efficiency of benzene. The gasoline fraction contains olefins and paraffins with 3 to 8 carbon atoms to the molecule.

CONSIDERABLE attention has been given recently to the possibility of utilizing gaseous hydrocarbons, such as natural gases and gases from oil-cracking plants, as sources of motor fuel of high antiknock value. Since the researches of Berthelot (*2*) which led to the first comprehensive theory of the mechanism of decomposition of hydrocarbons, many workers have demonstrated the conversion of aliphatic hydrocarbons into liquids essentially aromatic in nature. It is now seventy years since Berthelot began his researches on this subject and unproved steps are still to be found in all suggested mechanisms for the changes. Our knowledge of the mode of pyrolysis of even the gaseous hydrocarbons is still imperfect, but certain of the normal changes of these compounds, when subjected to heat, are now reasonably clear. Furthermore, in many cases it is possible to forecast with reasonable certainty the nature and the approximate quantities of the products obtained when even complicated gaseous mixtures are decomposed. Investigations on the laboratory scale, using pure single gases and synthetic mixtures, are largely responsible for these advances in knowledge.

From the industrial viewpoint, the production of liquid hydrocarbons from gaseous paraffins and olefins is of considerable importance owing to the vast quantities of these hydrocarbons available for development. In 1929 the quantities of paraffin hydrocarbons available, expressed in millions of cubic feet, were stated (*3*) to be: methane, 2,015,000; ethane, 336,150; propane, 111,415; and butane, 64,980. The quantities of gaseous olefins available are more difficult to estimate because of the considerable variation in the gases produced in cracking operations. A figure of 275,000 million cubic feet may be taken as the volume of cracker gas produced in 1930, and of this it is estimated that the quantities of gaseous olefin hydrocarbons available from this source, expressed in millions of cubic feet are: ethylene, 16,500; propylene, 22,000; butylenes 11,000.

From these figures it is estimated that the potential yield of benzene from the paraffins and olefins (methane excluded) by pyrolysis is of the order of 4,750,000 tons per year. Alternatively, if quantitative dehydrogenation of the paraffins to olefins and quantitative polymerization of the olefins to low-boiling liquid hydrocarbons are assumed, the potential liquid yield is 17,750,000 tons per year. On the assumption of 60 per cent efficiency for the two processes in combination, the yearly production would be reduced to 10,650,000 tons, but even this represents a quantity rather more than twice that produced by single-stage pyrolysis for aromatic hydrocarbons. Here, then, are two alternative schemes for the utilization of large quantities of gas with gasoline as the product; of the two, the second method is the more efficient and the more flexible, since by varying operating conditions it is possible to vary the products from butylene to lubricating oils.

The scope of Part I is a general review of work on the laboratory scale on the following processes: (1) pyrolysis for the production of motor benzene, (2) pyrolysis for the production of olefins, and (3) polymerization and condensation of olefins to give low-boiling liquids.

The term "pyrolysis" throughout this paper is confined to thermal treatments above 600° C. with the rates of flow used; for, although pyrolysis is a term of general application to the paraffins, with the olefins complications arise. The above operations are covered by patents (*1*).

While processes 1 and 3 are both of direct application to gas containing olefins such as gas from oil-cracking plants, natural gas must approach process 3 via mild pyrolysis for the production of olefins, or, as an alternative, via process 1. Figure 1 indicates the steps involved in these operations.

Mechanism of Decompositions

Paraffin Hydrocarbons. From their study of the action of heat on the unbranched chain paraffins from ethane to *N*-hexane the authors conclude that the degradation of these hydrocarbons proceeds by the reversible elimination of a molecule, HX, which may be either a paraffin of smaller molecular weight or, in the limit, hydrogen. The residue from this primary decomposition is an olefin. Thus with ethane, propane, and *N*-butane the primary decompositions are indicated by:

Ethane:
$CH_3CH_3 = CH_2{:}CH_2 + HH$
Propane:
$CH_3CH_2CH_3 = CH_2{:}CH_2 + CH_3H$
$CH_3CH_2CH_3 = CH_3CH{:}CH_2 + HH$
N-butane:
$CH_3CH_2CH_2CH_3 = CH_2{:}CH_2 + CH_3CH_2H$
$CH_3CH_2CH_2CH_3 = CH_3CH{:}CH_2 + CH_3H$
$CH_3CH_2CH_2CH_3 = CH_3CH_2CH{:}CH_2 + HH$

With each hydrocarbon the reactions are given in order of their importance. As the series is ascended, the tendency for hydrogen to be eliminated, leaving an olefin with the same number of carbon atoms as the original paraffin, rapidly diminishes.

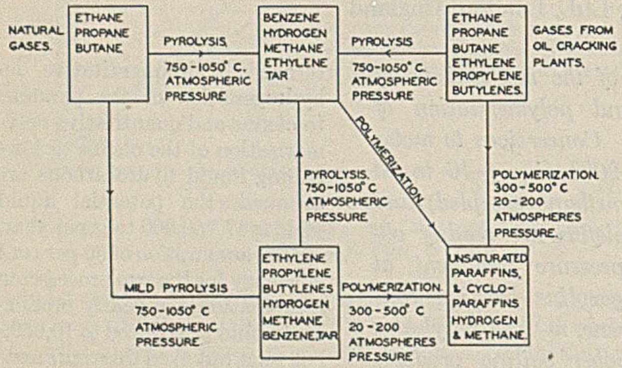


Figure 1. Steps in Pyrolysis and Polymerization Operations

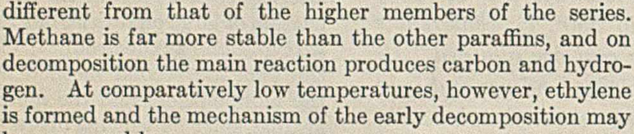
Methane requires separate consideration since the absence of a carbon-carbon linkage causes its behavior to be different from that of the higher members of the series. Methane is far more stable than the other paraffins, and on decomposition the main reaction produces carbon and hydrogen. At comparatively low temperatures, however, ethylene is formed and the mechanism of the early decomposition may be expressed by:

$$CH_3H \longrightarrow {=}CH_2 + HH$$

two of the CH_2 residues combining to form ethylene.

Above the range 700° to 750° C. under the conditions of these experiments benzene and other aromatic hydrocarbons are produced from each gas, methane included. Below this temperature range, when the primary reactions are taking place, each hydrocarbon follows its own course, but at the higher temperatures the secondary reactions are similar in all cases. At this stage of the syntheses, ethylene appears to be the starting point. The authors' experiments show that ethylene readily polymerizes to butylene, that butylene by dehydrogenation produces butadiene, that butadiene and ethylene unite in equimolecular proportions to give cyclohexene, and that cyclohexene produces benzene. The mechanism appears to be as follows:

$$2CH_2{:}CH_2 \longrightarrow CH_3CH_2CH{:}CH_2 \longrightarrow CH_2{:}CHCH{:}CH_2 + H_2$$



The exact mechanism of the addition of ethylene to butadiene is not clear, but cyclohexene has been shown to be an intermediate in the production of benzene. There are indications that a hexadiene precedes the production of cyclohexene and that a cyclohexadiene precedes the formation of benzene, but of this no satisfactory proof can be advanced as yet.

By analogy with the formation of diphenyl from benzene by condensation, it is reasonable to suppose that butadiene can condense with benzene to form naphthalene, and that anthracene and phenanthrene can be formed from naphthalene in a similar manner. Styrene, a product found in benzene produced by pyrolysis, may similarly be formed by the condensation of benzene and ethylene.

Olefin Hydrocarbons. With the olefins, ethylene, propylene, and the two unbranched chain butylenes, the principal primary changes, common to all, involve the formation of either the two-carbon or the four-carbon (or both) atom members of the olefin series. These reactions may be represented by:

Ethylene: $2C_2H_4 = C_4H_8$
Propylene: $2C_3H_6 = C_2H_4 + C_4H_8$
Butylene: $C_4H_8 = 2C_2H_4$

Butylene is not formed from ethylene by condensation to butadiene followed by hydrogenation; the change is a true polymerization. A secondary reaction which follows this polymerization is the elimination of hydrogen and the production of butadiene.

With propylene, an important secondary change, in the presence of hydrogen, is the production of methane and ethylene by scission of the carbon chain at the terminal carbon-carbon bond and subsequent hydrogenation of the radicals, as shown by:

$$CH_3CH{:}CH_2 + HH \longrightarrow CH_2{:}CH_2 + CH_3H$$

Of the two butylenes, Δ^{β}-butylene was found to be more stable than Δ^{α}-butylene. Three changes appear to be operative to approximately the same extent at 600° C. with the butylenes: (1) depolymerization to ethylene, followed by secondary hydrogenation of the ethylene to ethane, (2) scission of the carbon chain at the end single linking, with the formation of radicals which by hydrogenation give rise to propylene and methane, and (3) dehydrogenation of butylene to form butadiene.

At higher temperatures hydroaromatic liquid hydrocarbons are produced from the olefins by the general method of addition of butadiene and the olefin. This is followed by the elimination of hydrogen and the production of aromatic hydrocarbons.

Production of Aromatic Hydrocarbons from Pure Paraffins and Olefins on a Laboratory Scale. Under suitable conditions of temperature and contact time all the gaseous hydrocarbons produce quantities of liquid aromatic hydrocarbons. Furthermore, in the approximate temperature range 750° to 1100° C., the factors time and temperature are interdependent so that at the high temperatures it is possible, by adjusting the contact time, to obtain products similar to those at lower temperatures.

The effect of diluents on the production of aromatic hydrocarbons has been studied. Briefly, nitrogen is a true diluent and causes but a slow decrease in the production of aromatics with increasing concentration; oxygen in small quantities improves the yield of liquids, whereas hydrogen causes the formation of aromatics to fall off rapidly.

Some of the results obtained with a rate of flow of 4 liters per hour and a constant temperature reaction space of 52 cc. in a silica tube are given in Table I for the paraffins and in Table II for the olefins.

The pyrolysis of methane is an interesting problem. The conversion into benzene per pass through the reaction tube is low, but it is obvious that, if some economic method of hydrogen-removal could be found, the total conversion into benzene could be increased to perhaps 50 or 60 per cent of the methane supplied. Apart from the liberation of hydrogen and carbon, any hydrocarbon formed during the pyrolysis of methane would provide useful material for further pyrolysis. Carbon can be reduced to a minimum, and hydrogen-removal and utilization is the remaining problem. On the laboratory scale, hydrogen-removal could be accomplished by the use of copper oxide, but the problem is not solved commercially.

TABLE I. PYROLYSIS OF PARAFFIN HYDROCARBONS IN SINGLE-STAGE OPERATION FOR PRODUCTION OF AROMATICS AT ATMOSPHERIC PRESSURE[a]

PARAFFIN	TEMP.	CONVERSION TO LIQUIDS	CONVERSION TO GASOLINE BOILING BELOW 170° C. (338° F.)	CONVERSION Per 1000 cu. ft. total oils	CONVERSION Per 100 cu. m. total oil	CONVERSION Per 1000 cu. ft. gasoline boiling below 338° F.	CONVERSION Per 100 cu. m. gasoline boiling below 170° C.
	° C.	% by wt.	%	Imp. gal.	Liters	Imp. gal.	Liters
Methane	1050	8.8	5.0	0.44	7.1	0.25	4.0
Ethane	850	17.93	11.2	1.7	27.3	1.1	17.7
	900	21.9	10.63	2.1	33.6	1.0	16.0
Propane	850	23.09	11.65	3.25	52.1	1.6	25.6
Butane	800	20.4	12.91	4.0	64.3	2.4	38.5
	850	24.55	11.64	4.6	73.8	2.35	37.8
Pentane	850	26.8	11.87	..	..	..	..
Hexane	800	33.7	19.2	..	..	..	..
	850	33.8	19.0	..	..	..	..

[a] All conversions and yields are calculated on gas input and not on gas decomposed.

Various materials have been tested on the laboratory scale for use in the fabrication of tubes for large-scale pyrolysis. The main points when considering a material are that it (1) must be heat resisting, (2) should not be fragile, (3) should not be porous, (4) should inhibit carbon deposition, and (5) should encourage benzene production. Among the materials tested were silica, porcelain, graphite, copper, aluminum, iron, nickel, fireclay and a number of alloys, but not one of these materials proved perfectly satisfactory.

With the use of various metals and alloys is bound up the question of catalysis, and, in this, two separate factors are involved: (1) benzene formation and (2) carbon deposition.

Generally, these two factors are both unfavorable in a particular alloy or both favorable, but there are exceptions. Two of the best alloys are Ferralloy (14 per cent aluminum, 86 per cent iron) and H. R. 4 (26 per cent chromium, 0.3 per cent nickel, 1.5 per cent manganese, 0.9 per cent silicon, and 0.15 per cent carbon); the former is better than silica in inhibiting carbon deposition and encouraging benzene formation. There are indications to show that carburization takes place in a number of alloys and the catalytic properties may be affected.

TABLE II. PYROLYSIS OF OLEFIN HYDROCARBONS IN SINGLE-STAGE OPERATION FOR PRODUCTION OF AROMATICS AT ATMOSPHERIC PRESSURE[a]

OLEFIN	TEMP.	CONVERSION TO LIQUIDS	CONVERSION TO GASOLINE	CONVERSION Per 1000 cu. ft. total oils	CONVERSION Per 100 cu. m. total oils	CONVERSION Per 1000 cu. ft. gasoline boiling below 338° F.	CONVERSION Per 100 cu. m. gasoline boiling below 170° C.
	° C.	% by wt.	% by wt.	Imp. gal.	Liters	Imp. gal.	Liters
Ethylene	800	36.1	17.7	3.15	50.5	1.6	25.6
Propylene	750	35.6	20.4	4.7	75.4	2.75	44.1
	800	40.6	19.0	5.32	85.4	2.5	40.1
Δα-Butylene	700	35.8	23.6	6.25	100.2	4.1	65.8
	750	39.6	22.45	6.85	110.0	3.95	63.4
Δβ-Butylene	700	37.0	25.8	6.4	102.8	4.45	71.4
	750	39.6	23.2	6.85	110.0	4.1	65.8

[a] All conversions and yields are calculated on gas input and not on gas decomposed.

With the exception of the liquids from methane, it is found that 50 to 60 per cent of the total liquid hydrocarbons produced boil below 170° C., the chief constituent of this spirit being benzene. With methane, about 80 per cent of the liquid produced is benzene. When considering these figures, account must be taken of the small quantities of liquid treated and of the necessarily high handling losses. The spirit figures are, therefore, conservative estimates. Recent work has demonstrated that the term "spirit up to 200° C." means in practice 75 to 80 per cent of the "total liquids" recorded in the tables. On this basis, allowing 75 per cent, the figures become:

	CRUDE GASOLINE UP TO 200° C. Imp. gal./1000 cu. ft.	CRUDE GASOLINE UP TO 200° C. Liters/100 cu. m.		CRUDE GASOLINE UP TO 200° C. Imp. gal./1000 cu. ft.	CRUDE GASOLINE UP TO 200° C. Liters/100 cu. m.
Methane	0.3	4.8	Ethylene	2.4	38.5
Ethane	1.5	24.0	Propylene	3.9	62.5
Propane	2.4	38.5	Δα-Butylene	5.1	80.7
N-butane	3.4	54.5	Δβ-Butylene	5.1	80.7

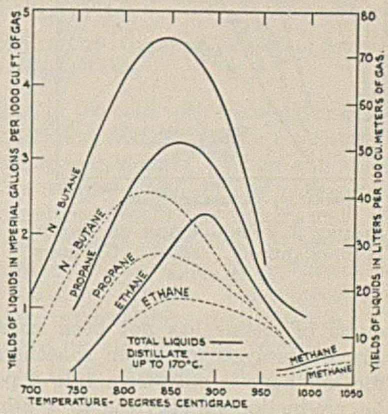


FIGURE 2. PRODUCTION OF LIQUID HYDROCARBONS FROM GASEOUS PARAFFINS

The experimental data are best indicated in graphical form (Figures 2 and 3). For one rate of flow—namely, 4 liters of gas per hour—the yields are expressed in liters of liquids per 100 cubic meters and Imperial gallons per 1000 cubic feet against the temperature of operation. This method of plotting has been adopted to present the results in a form directly comparable with large-scale operation. From Figures 2 and 3, and the corrected table of yields given, it is possible to calculate the approximate benzene production from a gas of known constitution. Thus, a gas obtained during the removal of gasoline, containing:

	%		%
Methane	2.8	Butane	39.6
Ethane	5.7	Pentane	2.3
Propane	49.8		

was expected to yield 2.7 Imperial gallons per 1000 cubic feet (43.3 liters per 100 cubic meters). In practice, on a semicommercial scale, the figure realized was 2.6 Imperial gallons per 1000 cubic feet (41.7 liters per 100 cubic meters).

CONDENSABLE PRODUCTS. The liquid products derived from pyrolysis operations may be conveniently divided into: (1) fraction boiling from 0° to 200° C. and (2) fraction boiling above 200° C.

The nature of the liquid hydrocarbons produced by pyrolysis has been shown to vary somewhat with operating conditions. In the region of optimum production of aromatic liquids, however, the variation is small and a representative example may be taken.

FRACTION BOILING FROM 0° TO 200° C. Up to 75 per cent by volume of this fraction was shown to be benzene itself. Toluene was present to the extent of 5 to 7 per cent. In the boiling range 135° to 150° C. the main constituent was shown to be styrene to the extent of 4 per cent of the gasoline fraction but *m*- and *p*-xylenes were also present. Indene was isolated and identified from the liquids boiling around 180° C. (For analysis made on the liquid product, see Part II, page 319.)

FRACTION BOILING ABOVE 200° C. From this fraction naphthalene, anthracene, and phenanthrene were readily isolated and identified, and the presence of chrysene was indicated.

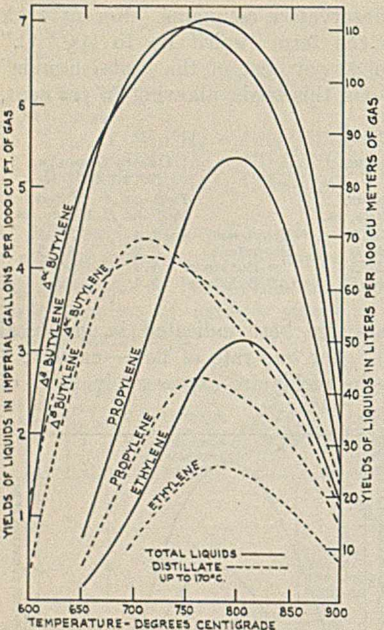


FIGURE 3. PRODUCTION OF LIQUID HYDROCARBONS FROM GASEOUS OLEFINS

PRODUCTION OF GASEOUS OLEFINS FROM PARAFFIN HYDROCARBONS. The lower paraffins present in natural gas provide a potential source of olefinic hydrocarbons by the application of mild pyrolysis. On the assumption of quantitative dehydrogenation of the paraffins Egloff, Schaad, and Lowry (*4*) have estimated the following production of olefins based on figures for 1929 and expressed in millions of cubic feet: ethylene, 218,700; propylene, 92,750; and butylenes, 59,980. This field is awaiting development.

Methane as a source of olefins has not been considered here, since in normal pyrolysis the olefin concentration in the exit gas from methane is only from 1 to 4 per cent. With ethane the production of ethylene is a primary reaction, and it is possible by suitable adjustment of the time factor at 900° C. to obtain a conversion into ethylene of 58 per cent (by volume) on the ethane pyrolyzed, or 67 per cent on the ethane decomposed by single-stage operation. Reference may here be made to the results of Cambron (*3*) which have shown an optimum conversion of 47.2 per cent on the ethane pyrolyzed or 90 per cent on the ethane decomposed.[1] Further development of this treatment is required, but a conversion, in single-stage operation, of 60 per cent by volume of ethane should be readily achieved.

By the mild pyrolysis of propane and butane it is possible to obtain 90 to 100 per cent conversion by volume into gaseous olefins. The increase in volume of the treated gas over the untreated is between 80 and 100 per cent. One experiment with *N*-butane at 700° C. is as follows:

Inlet gas rate, liters/hour	5.0
Outlet gas rate, liters/hour	9.9
Vol. of tube at reaction temp., cc.	52

Analysis by a Podbielniak gas analysis apparatus combined with separation of unsaturated and saturated components on the Bone and Wheeler gas analysis apparatus gave:

	PER CENT BY VOLUME	
	On exit gas	On inlet gas
Hydrogen	5.8	11.45
Methane	27.7	54.8
Ethane	7.8	15.4
Butane	11.85	23.4
Ethylene	23.5	46.5
Propylene	18.4	36.4
Butylenes	4.65	9.2

The butane used contained 97% by vol. *N*-butane, 3% propane.

This conversion is 92.1 per cent by volume on the *N*-butane passed through, or 120 per cent by volume on the butane decomposed. On a weight basis these conversions are 58 and 76 per cent, respectively.

INFLUENCE OF PRESSURE ON PYROLYSIS FOR AROMATIC HYDROCARBONS

From theoretical considerations the application of pressure to the pyrolysis of paraffin hydrocarbons is not sound, for the initial reaction must involve an increase in volume. This does not apply to the pyrolysis of olefins where, in the early stages, polymerization occurs.

The influence of pressure on the pyrolysis of the paraffins has only been considered experimentally in relation to ethane at pressures up to 150 pounds per square inch (10.5 kg. per sq. cm.) over the temperature range 700° to 800° C. The apparatus used consisted essentially of an electrically heated vertical reaction tube of a Hadfield, Ltd., special steel (H. R. 4) connected at the inlet end to a single-stage compressor capable of operating at pressures up to 200 pounds per square inch (14 kg. per sq. cm.) and at the outlet to three condenser receivers in series. After the condensers, pressure was reduced to atmospheric by means of a loaded ball valve which operated automatically at the set pressure. Gas was metered in and out of the apparatus, and liquid products were weighed and analyzed. The bore of the tube was 2.5 cm., and it was found that a length of 35 cm. was at constant temperature.

Under the conditions of experiment the maximum conversion into aromatic liquids was found at 750° C. and 150 pounds per square inch pressure when aromatic hydrocarbons corresponding to 12.4 per cent of the ethane passed through the reaction tube were obtained. Of these liquids about 50 per cent boiled below 150° C. The conversion at atmospheric pressure—namely, 22 per cent of the ethane pyrolyzed—was therefore not approached under the conditions considered. The formation of ethylene from ethane was apparently inhibited by pressure, and instead more ethane decomposed to methane, hydrogen, and carbon. The application of moderate pressure such as 50 pounds per square inch (3.5 kg. per sq. cm.) is sufficient to reduce considerably the olefin production and the quantity of aromatic hydrocarbons.

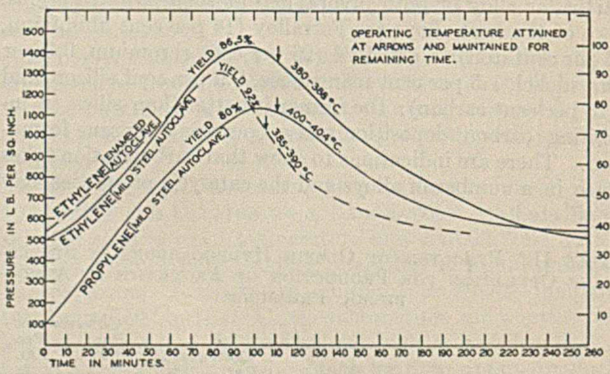


FIGURE 4. POLYMERIZATION OF OLEFINS IN AUTOCLAVES

The influence of pressure on the production of aromatic hydrocarbons from the olefins cannot immediately be deduced. The influence of pressures up to 150 pounds per square inch on the pyrolysis of ethylene has been studied experimentally over the temperature range 600° to 700° C. The highest recorded conversion into liquid hydrocarbons in this range is 35 per cent. By a suitable adjustment of the temperature and the time factor this figure may be approached at several pressures. The production of 36.1 per cent of liquid aromatic hydrocarbons at atmospheric pressure has not been improved upon, but the working temperature can be reduced by more than 100° C. by the application of pressure, without

---

[1] In a more recent communication [Cambron and Bayley, *Can. J. Research*, **9**, 175 (1933)] the conversion of ethane to olefins has been improved to 59 per cent on the ethane pyrolyzed by the use of baffled tubes.

loss of yield. Increasing the pressure in this temperature region appears to accelerate the deposition of carbon.

POLYMERIZATION OF OLEFINS

It has been shown that the first stage in the reactions involved when ethylene is heated at atmospheric pressure is a polymerization to butylene. Owing to the decrease in volume which occurs when gaseous olefins polymerize, increase in pressure favors the production of polymers. The case for polymerization and condensation as opposed to pyrolysis for the production of aromatic hydrocarbons is strong and may be indicated as follows:

PYROLYSIS	POLYMERIZATION AND CONDENSATION
(1) High temperatures (800° to 1100° C.) render necessary the use of expensive special steels.	Temperatures are comparatively low (up to 500° C.)
(2) Operation at or near atmospheric pressure is advisable with necessity for large plant.	Pressures higher than atmospheric are an advantage, and consequently plant size is reduced.
(3) Comparative low yields of liquid suitable for motor benzene are obtained.	Yields of liquid hydrocarbons approach theoretical (up to 92 per cent).
(4) Deposition of carbon appears inevitable.	Under suitable conditions carbon deposition is negligible.
(5) Production of tar is large.	Tar production is negligible.
(6) Dilution with hydrogen may considerably reduce yields obtainable.	Dilution with hydrogen has no considerable influence on production under suitable conditions.

While this comparison is of direct application to olefins only, it is rendered applicable to natural gas hydrocarbons through the medium of mild pyrolysis. Under conditions less drastic than those necessary for aromatic production by 100° to 150° C., it is possible to achieve high conversions of paraffins into olefinic hydrocarbons with elimination of trouble due to carbon and tar fog formation. To a large extent, also, the steel difficulties are obviated since the temperature range is now reduced to that common in industrial operations such as the methane-steam reaction. The gas produced by the operation of mild pyrolysis resembles gas obtained by the cracking of oil in the vapor phase and contains 40 to 50 per cent by volume of olefins, the rest being saturated hydrocarbons and hydrogen. Under these circumstances it is essential to the application of polymerization that dilution with inert paraffin gases should not interfere considerably with the conversion into liquid polymers. In commercial operation it may be advisable to reduce the load on the plant by elimination of such gases as hydrogen and methane after compression of the mixed gas.

The polymerization of the gaseous olefins has been studied in three different pieces of apparatus: (1) autoclaves, (2) a continuous plant supplied from cylinders of compressed gas, and (3) a continuous plant using a compressor, briefly described previously in the section on the influence of pressure on pyrolysis for aromatic hydrocarbons.

Of these the pressure limit of apparatus 1 and 2 was 2000 pounds per square inch (140.6 kg. per sq. cm.) and of 3, 200 pounds per square inch (14 kg. per sq. cm.).

AUTOCLAVES

Two mild steel autoclaves were used in this part of the work, one of 500 cc. capacity and the other 750 cc. Of these, the latter was carefully enameled internally so that no steel was presented at operating temperature to the hydrocarbon gas. These autoclaves were heated in a specially designed gas furnace in which the heating gases were circulated by a fan, and it was possible to maintain a steady temperature in the autoclave within ±2° C. over long periods of time. Each autoclave had a long tube of small internal diameter supporting the valve, pressure gage, and safety disk at a sufficient distance from the body of the autoclave to be quite cool. The thermocouple pocket in each autoclave was fitted in the lid. Metal-to-metal joints of the cone type were used throughout, and these could be made and broken usually about fifty times before refacing became necessary.

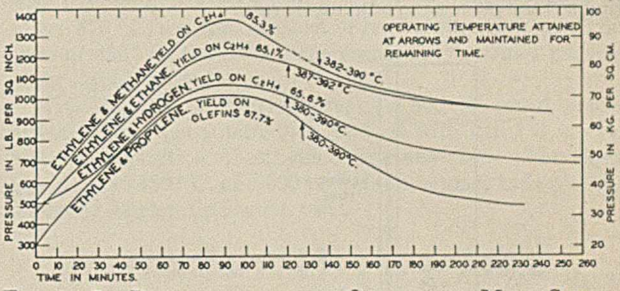


FIGURE 5. POLYMERIZATION OF OLEFINS IN MILD STEEL AUTOCLAVE

The autoclave was filled in the cold with the olefin or gaseous mixture under consideration, and charges were measured by use of a balance weighing to 0.05 gram. Where a mixture was being made up with a saturated gas, such as methane or ethane, the olefin was introduced first and notes were made of the weight added and the pressure when cold. It was then possible, by filling to a calculated pressure, to approach the desired composition of mixture. Finally, this composition was determined accurately by reweighing the autoclave.

The time-pressure curves for ethylene and propylene are shown in Figure 4 and the results summarized in Table III.

TABLE III. PRODUCTION OF LIQUID HYDROCARBONS FROM OLEFINS

CHARGE	VOLUME PROPORTIONS	TEMP.	MAX. PRESSURE		TIME AT WORKING TEMP.	CONVERSION INTO LIQUIDS
	%	° C.	*Lb./sq. in.*	*Kg./sq. cm.*	*Hours*	*% by wt. on olefin changed*
Ethylene	..	380–388	1410	99.1	3	86.5
Propylene	..	400–404	1010	71	2.5	80.0
Ethylene Propylene	58 42	390–400	1010	71	3.5	87.7
Ethylene Hydrogen	49.2 50.8	380–390	1040	73.1	3	65.6
Ethylene[a] Methane	51.5 48.5	382–390	1390	97.7	3	85.3
Ethylene Ethane	49.2 50.8	387–392	1220	85.8	2.5	65.1
Ethylene[b]		385–390	1325	93.1	3	92

[a] A possible explanation of the high yield of liquid is that dilution with methane tends to repress the production of methane during reaction.

[b] In enameled autoclave.

With olefins alone, or mixed with saturated gases, the pressure increased as heating progressed and attained a maximum in the region 340° to 375° C.—that is to say, before the reaction temperature was reached. Subsequently, the pressure fell with time when the autoclave was maintained at the reaction temperature, rapidly at first and then more slowly until the pressure drop with time became negligible. The experiment was then stopped and the autoclave allowed to cool.

With ethylene at 400° to 404° C. and pressures of 1200 pounds per square inch (84.4 kg. per sq. cm.) the rate of drop in pressure was very rapid, of the order of 60 pounds per square inch (4.2 kg. per sq. cm.) per minute. In one experiment, under these conditions, a conversion of 73.2 per cent by weight into liquid products was obtained; 39 grams of ethylene produced 28.55 grams of liquid and 6.71 liters of residual gas. The residual gas contained only 15 per cent unsaturated hydrocarbons, and it would appear that these conditions were too drastic for complete conversion to polymers. The temperature range 380° to 392° C. was therefore used in later autoclave work with ethylene. In Figure 4 the differences between a mild steel surface and an enameled surface are clearly seen. The rate of reaction, as indicated by the pressure drop in unit time, was greater with the enameled surface, and the yield of liquid hydrocarbons was the highest reported (92 per cent by weight) and carbon deposition was negligible.

It is of interest that propylene required a temperature approximately 10° C. higher than ethylene to cause polymerization to take place at a comparable rate.

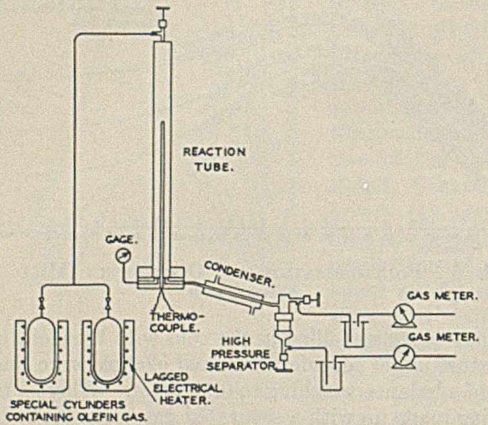


FIGURE 6. POLYMERIZATION APPARATUS

The next step in the development of polymerization work in autoclaves was a consideration of the influence of diluents, including therein other olefins, on the polymerization of ethylene.

The first mixture made up was 1 to 1 by weight of ethylene and propylene, followed by a preliminary investigation of hydrogen, methane, and ethane as diluents. The results are summarized in Table III, and time-pressure curves are given in Figure 5, from which it is obvious that none of the diluents reduced the conversion into liquids below 65.1 per cent by weight. These experiments demonstrated the possibility of treating gas rich in olefins, such as gas from an oil-cracking plant or gas from the mild pyrolysis of natural gas, without previous elimination of hydrogen and saturated hydrocarbons. In practice it would be necessary to consider the economics of such a procedure by balancing the cost of any desired purification against the cost of the extra plant necessary to deal with the whole of the gas.

CONTINUOUS PLANT. For many reasons an autoclave is not a suitable apparatus for effecting the polymerization of olefins; thus, the pressure is not constant and the reaction rate slows up with fall in pressure, while the products remain in the heated zone for a considerable period and suffer change with the deposition of carbon and the production of saturated gases. The next development, therefore, was a simple type of continuous plant with a reactor of tubular form so that lining tubes of different materials could be fitted.

A drawing of the plant is shown in Figure 6. It consisted of a mild steel reaction tube 123.5 cm. long and of 2.5 cm. internal diameter, supported vertically and fitted at the top with an inlet tube and valve and at the bottom with a long axial thermocouple pocket, a gage, and an outlet leading through a condenser to a high-pressure separator of 188 cc. capacity. The tube was electrically heated by a double winding applied to it over mica insulation, giving a distance of 25 cm. at constant temperature within ±1.5° C. Metal temperatures were taken by two thermocouples brazed into small screwed pockets. Ethylene was supplied to the plant from one of two special gas cylinders connected in parallel to a fine adjustment valve at the top of the reaction tube. These cylinders could be warmed in lagged electrical heaters.

Pressures in the tube reactor were controlled by hand adjustment of the valve on the cylinder and the fine adjustment valve at the top of the reaction tube. As the pressure dropped, more gas was admitted from the cylinder to maintain the operating pressure.

From the high-pressure separator, liquid could be withdrawn to a cooled receiver and gas could be vented through a condenser to a gas meter. Normally it was possible to operate this plant without venting gas—that is to say, without the production of any considerable quantity of saturated gases. In this way gas was taken off at the conclusion of an experiment, measured, and sampled. It was usually sufficient to determine the percentage of olefins using the Bone and Wheeler gas analysis apparatus, but occasionally Podbielniak analyses, accompanied by absorption on the Bone and Wheeler apparatus, were carried out.

The conversion figures were readily determined by weighing the liquid polymers and the gas cylinders before and after an experiment.

Mild Steel Surface. With a surface of mild steel at 380° to 390° C. and 800 pounds per square inch (56.2 kg. per sq. cm.) pressure the polymerization of ethylene was rapid, and conversions up to 64 per cent on the ethylene supplied were recorded. Unfortunately, it was found that the carbon formation under these conditions represented 6.6 per cent of the weight of the liquids obtained, and, even when the temperature was reduced to 360° C., where polymerization was slow, the carbon deposition was not considerably reduced.

Other Surfaces. Various lining materials were tried, including copper, aluminum, stainless steel, and two steels of differing composition which proved reasonably satisfactory—namely, Era 131, or containing 0.3 per cent manganese, 0.5 per cent chromium, 0.5 per cent copper, 0.7 per cent molybdenum, 0.1 per cent carbon, and a heat-resisting steel known as H. R. 2, containing 22 per cent chromium, 7 per cent nickel, 1.5 per cent silicon, and 0.15 per cent carbon.

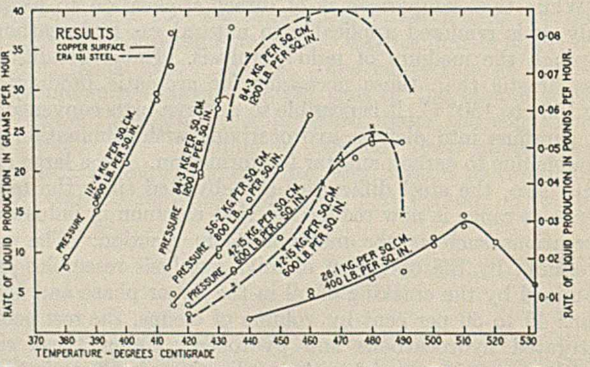


FIGURE 7. INFLUENCE OF PRESSURE ON RATE OF PRODUCTION OF LIQUID HYDROCARBONS IN THE POLYMERIZATION OF ETHYLENE

Lining tubes of copper and Era 131 steel.

Using a lining tube of copper it was found that at a pressure of 800 pounds per square inch it was necessary to operate at 440° C.—that is to say, 50° to 60° C. higher than when using mild steel to obtain comparable reaction rates. The liquid hydrocarbons produced under these conditions gave Engler distillation figures of:

Initial boiling point, ° C.	40
Distillate to 50° C., %	2.5
75	12
100	27.5
125	43.5
150	57.5
175	71
200	79
300	95
303	96.5
Residue, %	1.6
Loss, %	1.9

Following this preliminary test of copper as a lining, tests with other materials were carried out at varying temperatures from 370° to 530° C., and at pressures from 200 to 2000 pounds per square inch (14 to 140.6 kg. per sq. cm.). Some of the results are summarized in Table IV and expressed graphically in Figure 7. As the pressure was increased, the temperature necessary to attain a given rate of production of liquid decreased.

At pressures of 400 and 600 pounds per square inch (28.1 and 42.2 kg. per sq. cm.) the curves obtained (Figure 7) pass through a maximum point, whereas at pressures above 600 pounds per square inch, such points are not attained with lining tubes of copper. The explanation of this is that at pressures of 800 pounds per square inch (56.2 kg. per sq. cm.) and higher, violent decomposition of the olefin (resembling the flashing of acetylene) occurred, accompanied by a copious deposition of soft carbon. The external evidence of this phenomenon was a rapid rise in temperature accompanied by a very rapid increase in pressure. Thus it is not advisable to employ copper liners in polymerization experiments above a pressure of 600 pounds per square inch unless the temperature is kept low and the attainment of the optimum conversion rate is not attempted. This violent decomposition of ethylene occurred both with an oxidized copper and a cleaned copper surface.

Conversion figures up to 85 per cent were obtained, but this was not a maximum, since it was not possible to account for all the ethylene passed into the apparatus. No material improvement in production is obtained by increasing the copper surface in the reaction zone by packing with Lessing rings.

A Podbielniak analysis of the residual gas after operation at 800 pounds per square inch and 445° to 450° C. gave:

	%
Uncondensed (methane and hydrogen)	5.1
Ethylene	58.4
Propylene	10.0
Butylenes	16.0
Amylenes	10.0

so that only small amounts of saturated hydrocarbons were being produced under these conditions.

In this continuous plant, the influence of nitrogen as a diluent was considered by first filling the apparatus with nitrogen to a pressure of 400 pounds per square inch (28.1 kg. per sq. cm.). Ethylene was then admitted until the operating pressure of 800 pounds per square inch was attained. No gas was allowed to escape from the system until the conclusion of the experiment. From a series of experiments with nitrogen and ethylene, it was concluded that the partial pressure of the ethylene controlled the rate of production of polymerides.

Table IV. Polymerization of Ethylene

Pressure	Temp. Range for Liquid Production	Apparent Optimum Temp.	Rate of Liquid Formation[b]	Remarks
Lb./sq. in. (kg./sq. cm.)	*° C.*	*° C.*	*Vol./vol. reaction space/hr.*	
		reactor with copper lining tube		
400 (28.1)	420–540	510	0.27	....
600 (42.2)	400–500	480	0.46	....
800 (56.2)	390–460	460[a]	0.53	Violent decompn. above 460° C.
1200 (84.4)	380–440	430–440[a]	0.73	Violent decompn. above 435° C.
1600 (112.5)	360–415	410–415[a]	0.73	Violent decompn. above 415° C.
		reactor with lining tube of era 131		
600 (42.2)	400–500	480	0.49	
1200 (84.4)	380–500	470	0.79	

[a] These are not true values owing to interference, due to deposition of soft carbon at these temperatures before the maximum conversion is attained.

[b] At apparent optimum temperature.

Both the Era 131 and H. R. 2 steels showed distinct advantages over copper as lining tubes.

The results of two series of experiments with Era 131 are given in Table IV for comparison with the results using a copper liner and are indicated graphically in Figure 7. At the lower pressures, copper and Era 131 resemble each other but, at pressures of 800 pounds per square inch and above, no violent decomposition is observed when using Era 131. Thus even at 1200 pounds per square inch pressure it is possible to pass through the maximum conversion rate without interference due to violent decomposition; and, whereas at this pressure the temperature range with copper is limited to 380° to 440° C., and at the higher temperature violent decomposition occurs, with Era 131 the range is 380° to 500° C., with maximum conversion rate at 470° C. At temperatures above 470° C. a surface deposit of hard carbon is formed, but even at 490° C. the carbon represents only about 1 per cent of the liquids produced.

With H.R.2 steel, temperatures over 500° C. could be used at 600 pounds per square inch, and, as with Era 131, no violent decomposition of ethylene was observed. The liquid produced at 480° C. and 600 pounds per square inch gave the following Engler distillation test:

Initial boiling point, ° C.	20
Volume to 25° C., %	Few drops
50	9.2
75	25.5
100	42.5
125	58.0
150	70.0
175	80.0
200	86.0
225	89.5
250	92.0
275	94.0
Final boiling point, ° C.	278

Continuous Plant Using Compressor. This apparatus was designed for operation up to a pressure of 200 pounds per square inch (14 kg. per sq. cm.) for a study of the problem of pressure as applied to pyrolysis, and the plant has been briefly described in the section of this paper dealing with that subject. With ethylene in the pressure region 150 to 200 pounds per square inch (10.5 to 14 kg. per sq. cm.) this plant was useful in indicating that 550° to 600° C. is a transition region in that, above this range, the liquids produced are largely aromatic in constitution, whereas below this range polymerization occurs and the liquids are largely paraffinic and olefinic in nature.

Time Factor in Polymerization of Ethylene. With regard to the time factor in the polymerization of ethylene, a statement of the volume of the reaction space at constant temperature accompanied by the curves in Figure 7 are sufficient for the purpose of transferring these operations to a larger scale. The required volume, after making allowance for the thickness of the lining tube and the cover (of the same material as the liner) placed over the mild steel thermocouple pocket was 68.7 cc. Using a liner of H.R.2 steel at 1100 pounds per square inch (77.3 kg. per sq. cm.) and 470° C., a reaction space of about 0.1 cubic foot is required for the treatment of 50 cubic feet (0.1 cubic meter for 50 cubic meters) of ethylene (measured at normal temperature and pressure) per hour. Expressed in a different manner, it is found that, if the volume of ethylene reacting is corrected by the ordinary gas laws for temperature and pressure and the contact time is taken as the number of minutes required for unit volume of ethylene (so corrected) to pass through unit volume of reaction zone, a figure of about 3 minutes is obtained. The deviations from the gas laws are considerable and no account is taken of volume change during reaction. It is thought that the former method of expression is preferable.

Liquid Hydrocarbons Produced by Polymerization and Condensation

The crude liquid from autoclave operation is turbid and dark in color; 60 to 70 per cent of it boils below 200° C., and 88 to 93 per cent below 300° C., depending upon operating conditions. Engine tests of the liquid boiling below 200° C. indicate that the antiknock value as a fuel is about half that of benzene. The liquids produced in the "dilution" experiments, where the diluent was not another olefin, were invariably lighter in color than those obtained from the olefins alone, and the quantity of carbon was considerably reduced.

The liquid hydrocarbons from the continuous plant possessed a light straw color and were quite transparent. The boiling range of these liquids varied with the conditions of temperature and pressure of their production, but the usual product had a specific gravity of 0.75 to 0.77 at 15° C., and 80 to 86 per cent distilled below 200° C. The liquids obtained using a copper lining tube have been fractionated four times through a short but efficient spiral fractionating column, and the distillation curve of the liquids boiling up to 150° C. is given in Figure 8. "Steps" occur at 37° to 39°, 64° to 66°, 94° to 98°, 100°, and 120° C. These steps, together with the evidence supplied by gas analysis, indicate the presence of olefins or paraffins, or both, containing from 3 to 8 carbon atoms to the molecule. Thus, from gas analyses, propylene, the butylenes, and the amylenes are present. Furthermore, the percentage unsaturation of the liquid fractions has been estimated and it has been found that this decreased with rise in temperature from 75 to 80 per cent in the region of 39° C., to 50 per cent in the 120° C. range. Thus the polymerides are largely olefinic, with an increasing proportion of paraffins as the boiling point increases. All fractions were stable when exposed to sunlight and gave no reaction with maleic anhydride. These facts are taken as evidence that hydrocarbons containing conjugated double bonds in the molecule were absent. There are indications of the presence of naphthenes.

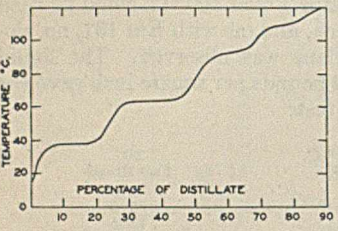


FIGURE 8. FRACTIONAL DISTILLATION OF LIQUID BOILING UP TO 120° C. IN THE POLYMERIZATION OF ETHYLENE

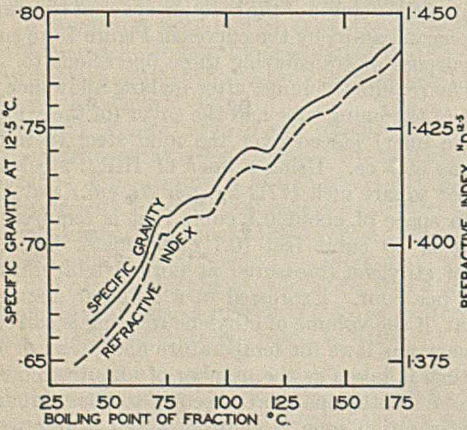


FIGURE 9. RELATIONSHIP BETWEEN SPECIFIC GRAVITY AND BOILING POINT, AND REFRACTIVE INDEX AND BOILING POINT AFTER FRACTIONATION INTO 2° C. CUTS IN THE POLYMERIZATION OF ETHYLENE

The specific gravities and refractive indices of the 2° C. cuts obtained by fractionation, plotted against boiling point, are shown in Figure 9.

In Figure 10 the results of several experiments on the solubility of ethylene in polymers are indicated graphically. This information was necessary to obtain some idea of the loss of the ethylene due to solubility in the polymers when the latter were withdrawn from the separator, and also to indicate the influence of temperature on this solubility.

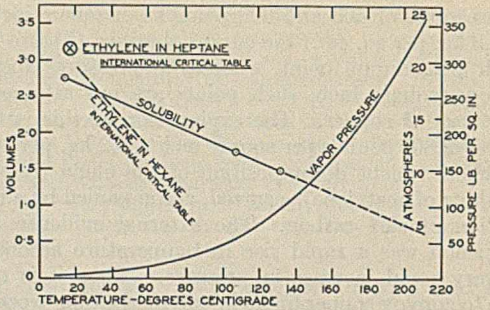


FIGURE 10. SOLUBILITY OF ETHYLENE IN POLYMERS

Volumes (at normal temperature and pressure) in one volume of solvent per atmosphere of partial pressure; Bunsen's absorption coefficient, ∞.

ANTIKNOCK VALUES

It has been stated that engine tests using 30 per cent blends of polymer from autoclave operation with standard stock indicated that the polymer gasoline, up to 200° C., was about half as effective as benzene. The antiknock value of the polymerides is considerably increased by operation in a continuous plant, and in 30 per cent blends the gasoline fraction was five-sixths as good as benzene on a volume relationship. These tests were carried out on the Armstrong engine. The gasoline tested had Engler distillation figures as follows:

Sp. gr. at 59.5° F. (15.3° C.)	0.745
Initial boiling point, ° C.	36
Distillate at 50° C., %	1.5
75	17.5
100	37.0
125	56.0
150	73.5
175	88.5
200	96.5
Final boiling point, ° C.	212
Distillate, %	98
Residue, %	1.2
Loss, %	0.8

When considering the engine test results of the low-boiling polymers from ethylene, attention must be drawn to the specific gravities of the liquid hydrocarbons concerned. On a weight basis it seems reasonable to suppose that the polymers form a rather better antiknock material than benzene.

DIESEL FUEL

It will be of interest to produce from the olefin polymers a fraction suitable for use as a diesel fuel. There is reason to suppose that the higher boiling polymerides will constitute a good diesel fuel. Tests are now in progress.

ACKNOWLEDGMENT

The authors are grateful to the directors of the Anglo-Persian Oil Company, Ltd., for allowing publication of the work described in this paper. Acknowledgment must also be made for the assistance in the work of F. Booley, W. A. Hayward, and W. L. Wood.

LITERATURE CITED

(1) Anglo-Persian Oil Co., British Patents 309,455 (April 8, 1929); 327,715 (April 7, 1930); 385,981 (Jan. 9, 1933).
(2) Berthelot, *Compt. rend.*, 62, 905, 947 (1866); 63, 788, 834 (1867); *Bull. soc. chim.*, [2] 7, 217 (1867); *Ann. chim. phys.*, 9, 471 (1866).
(3) Cambron, *Can. J. Research*, 7, 646 (1932).
(4) Egloff, Schaad, and Lowry, *J. Phys. Chem.*, 34, 1617 (1930); 35, 1825 (1931).

RECEIVED September 7, 1933.

II. Semi-Industrial Production of Aromatic Hydrocarbons from Natural Gas in Persia

W. H. Cadman, Anglo-Persian Oil Company, Ltd., London, England

The work described in Part II deals with the pyrolysis of natural gas at the oil fields in Persia on a semi-commercial scale for the production of liquid aromatic hydrocarbons. It was done simultaneously with the more academic research on the thermal decomposition of pure hydrocarbons described in Part I. The whole of this work was planned primarily in connection with the utilization of natural gas in Persia. The yields of benzene under varying conditions of temperature and pressure were found and optimum conditions determined.

The method of desulfurizing the gas is described, and the various furnaces and retort materials which were tested in the experiments are reviewed. Special heat-resisting alloy steel tubes in a radiant heat type of furnace were found to stand up best, but the ideal long-life metal for an industrial pyrolysis plant has yet to be found. It is pointed out that the chemist in this field is ahead of the metallurgist.

Attention has to be paid to the catalytic action of the material on the gases, which influences both benzene formation and carbon deposition in the reaction tubes. The importance of turbulent flow is emphasized.

The reaction products identified were: benzene, toluene, xylene, styrene, indene, naphthalene, anthracene, phenanthrene, chrysene, butadiene, and isoprene. The gases remaining after benzene production contained about 20 per cent of ethylene, which is a potential source of further liquid hydrocarbons.

Since the experiments described in this paper were completed our knowledge of the art of pyrolyzing hydrocarbon gases has advanced considerably, and further development work on a semi-commercial scale is now in progress.

FROM the industrial viewpoint the production of liquid aromatic hydrocarbons from gaseous paraffins and olefins is of considerable importance owing to the vast quantities of these hydrocarbons available for development. In 1929 the quantities of paraffin hydrocarbons available, expressed in millions of cubic feet, have been stated to be: methane, 2,015,000; ethane, 336,150; propane, 111,415; and butane, 64,980 (in millions of cubic meters: methane, 57,059; ethane, 9516; propane 3127; and butane 1840). The potential production of aromatic gasoline from these gases, methane excepted, is 2,950,000 tons per year or 8100 tons per day.

In Persia the natural gases are designated as follows:

(1) High-pressure gas is that part taken from the high-pressure separators operating under the natural pressure of the oil.

(2) Low-pressure gas is separated from the crude oil when the latter is reduced to approximately atmospheric pressure. This separation is made in flow tanks at 3 to 6 inches of water pressure.

(a) Unstripped gas is low-pressure gas which has not had its gasoline removed by absorption or compression.

(b) Stripped gas is low-pressure gas from which gasoline has been removed.

(3) Accumulator gas is obtained during the removal of gasoline and consists mainly of propane and butane.

These gases vary in composition with operating conditions in the oil field and seasonal changes, but approximate analyses made on a Bone and Wheeler apparatus, and subsequently confirmed by a Podbielniak apparatus, when the work to be described was in progress are:

	High-Pressure Gas	Unstripped Low-Pressure Gas	Stripped Low-Pressure Gas	Accumulator Gas
	%	%	%	%
H_2S	4.0	12	12	11.5
Methane	76	29	40	2.5
Ethane	18	24	21	5.0
Propane	1	21	18	44.0
Butane	1	10	9	35.0
Pentane+	..	4	Trace	2.0

The quantities of these gases available vary with the production of crude oil but are of the order of 142,000 cubic meters (5,000,000 cubic feet) per day of high-pressure gas; 852,000 cubic meters (30,000,000 cubic feet) per day of unstripped low-pressure gas of which 681,600 cubic meters (24,000,000 cubic feet) per day appear as stripped, hydrogen sulfide–free, low-pressure gas, and 5,000,000 cubic feet per day of gas corresponding approximately to accumulator gas.

From considerations of the quantity and constitution of high-pressure gas the development work was carried out on low-pressure and accumulator gases, since these richer gases presented better prospects of successful commercial development.

THE HYDROGEN SULFIDE PROBLEM

From the analyses given, it will be observed that natural gas from the Persian oil fields contains large quantities of hydrogen sulfide, and for the purpose of pyrolysis for the production of aromatic hydrocarbons it is essential that the hydrogen sulfide content should be considerably reduced. Two considerations for permissible hydrogen sulfide content are involved: (1) life of plant materials and (2) sulfur content of benzene produced. Operating with unpurified gas caused excessive corrosion of the heating tubes and contamination of the liquid products with carbon disulfide, thiophene, and traces of mercaptans. Thus, using unpurified stripped gas, a liquid product containing 7 to 8 per cent sulfur was obtained. Using undesulfurized gas, it is interesting to note that a product resembling rubber was obtained from the cooling mains on opening these after pyrolysis. The permissible maximum hydrogen sulfide content is probably in the region of one per cent.

Desulfurization may be carried out by one or more of the following methods:

(1) Partial oxidation by means of a Claus-Chance type plant.

(2) Washing with sodium sulfide solution and reactifying the solution with air.

(3) Water-washing the gas under pressure.

(4) Other methods including (a) Koppers sodium carbonate process, (b) triethanolamine, (c) alcohol or glycerol.

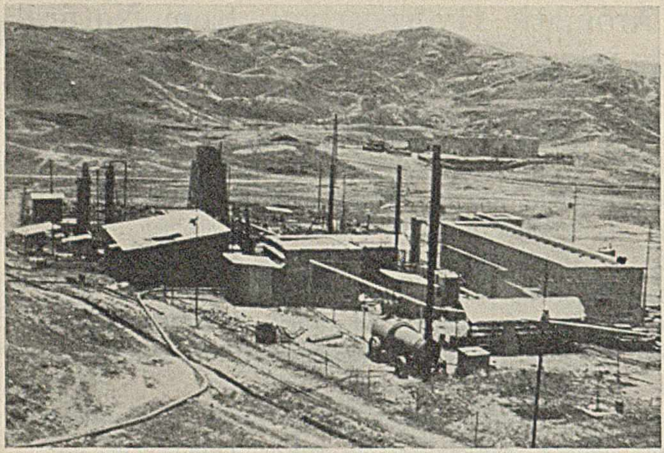


Figure 1. First Benzene Production Plant of the Anglo-Persian Oil Company in Persia

Condensers, in which a rubber-like material (latex) accumulated, are shown to the right of the portable steam boiler.

A detailed account of methods of desulfurization would be misplaced, but, to appreciate the operation of the semilarge-scale pyrolysis plants in Persia, it is necessary to outline briefly the process used for this purpose.

It was desirable to have a sulfur recovery plant and the partial oxidation process depending on the reaction:

$$2H_2S + O_2 \longrightarrow 2S + 2H_2O$$

was developed. The plant consisted of a preheater in which the temperature of the gas was raised up to about 300° C. (572° F.); a mixing chamber where the necessary air was introduced; a catalyst-filled reaction chamber; and a glass-wool sulfur fog extractor. By this operation the hydrogen sulfide content was reduced from 12 per cent to 1.5–2 per cent by volume. Two serious objections could be raised against this method of hydrogen sulfide removal: (1) a second plant of the countercurrent wash type was necessary to complete the desulfurization, and (2) the method loaded the pyrolysis plant with about 25 per cent by volume of nitrogen.

The other methods of hydrogen sulfide removal need not be discussed since they have been thoroughly worked out elsewhere.

Layout and Method of Operation of Plant

When natural gases are subjected to high temperatures under controlled conditions for the purpose of benzene formation, complex thermal decomposition of the gaseous hydrocarbons takes place resulting in the production of gases, liquid aromatic hydrocarbons, tar, naphthalene, and carbon. Furthermore, it has been shown that the presence of a large quantity of hydrogen sulfide is highly destructive to metal furnace materials and has a deleterious effect on the product. For the treatment of Persian natural gases a pyrolysis plant therefore consists of:

Plant for removal of hydrogen sulfide.
Pyrolysis furnace and reaction chamber.
Cooler and tar eliminator.
Naphthalene scrubber.
Plant for removal of tar fog.
Benzene recovery plant.
Refining plant.

In the large-scale development work in Persia (Figures 1 and 2) the layout of the various plants followed the lines of the general statement indicated above. A line diagram of general application to the plants used, but omitting the desulfurization and refining sections, is given in Figure 3. After the furnace is seen a lagged reaction chamber; this was fitted with baffles but was not externally heated. This reactor was equivalent to a definite length of tube in the furnace, and its use was largely a question of equating cost of reactor to the cost of the equivalent quantity of what may be expensive special metal tubes. After the heating section the gas passed to a combined water-spray cooler and tar leg in which the gas temperature was reduced from 800–850° C. (1472–1562° F.) to about 90° C. (194° F.) and the bulk of the tar was removed. Thence the gas passed to a warm tar scrubber for naphthalene removal followed by a glass-wool filter for removal of tar fog. This method of tar fog removal was quite satisfactory as was the alternative form, tried out on the plant, of electrical precipitation. Before reaching the recovery plant, the gas was cooled in a series of film coolers. The benzene recovery plant was of the usual type of oil absorption followed by distillation.

The main line of research resolved itself into the testing of various furnace designs and materials from the viewpoints of satisfactory life at high temperatures, production of benzene, and efficiency of heat transfer. The plant was controlled by the specific gravity of the exit gas as determined at short intervals of time by use of the Edwards balance. With one gas feed, runs were made at decreasing exit specific gravities, and one gravity was held for approximately 24 hours before passing on to more drastic conditions. This method was followed unless the pressure drop across the furnace indicated excessive carbon deposition, when the plant was shut down for cleaning. It was found that thermocouple pyrometers often failed owing to radiation troubles and deposition of carbon on the pyrometer pockets. Optical pyrometers were used for reading the furnace temperatures.

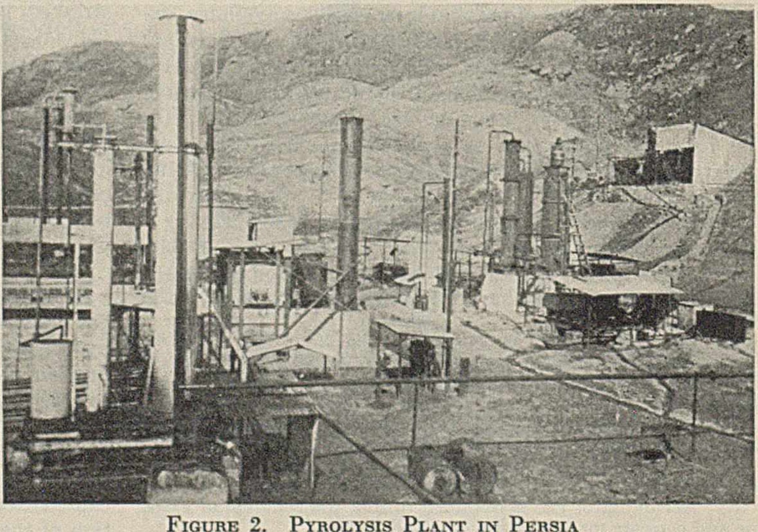


Figure 2. Pyrolysis Plant in Persia

Left, recovery unit; center, recuperative furnace; right, desulfurization plant with the Claus-Chance plant on the hillside.

Fire Clay

For operation at temperatures in the region of 800° to 1200° C. (1472–2192° F.) fire clay was one of the first materials thought of for the construction of retorts and tubes for commercial development. A suitable fire clay will both withstand the temperature necessary for benzene production for long periods and also restrain the tendency of the hydrocarbon treated to decompose to carbon. Against any advantages, however, must be set the necessity of using comparatively thick-walled retorts to obtain the necessary strength. In this tubular form, therefore, heat transfer is decidedly bad and large furnaces are required, whereas, if the wall thickness is reduced to improve heat transfer, the tubes become very fragile. Pressure cannot be used with fire clay tubes, and there is difficulty in constructing gas-tight joints.

A brief account of the experimental work with fire clay retorts and tubes will be given here, since this was the material which first indicated the order of benzene yield to expect from a large-scale operation in Persia.

The furnace setting used with the fire clay tubes was built by British Furnaces, Ltd., and housed six fire clay retorts each 3 meters (10 feet) long [made from 1.5-meter (5-foot) lengths fitted with sleeves and joints cemented with fire clay]. Refractory tubes of different diameters and thicknesses were tested varying from 22.9 to 7.3 cm. (9 to 3 inches) i. d., and having wall thickness varying from 7.6 to 1.9 cm. (3 to 0.75 inch). The retorts were first arranged in parallel so that any one could be cut out at will. A normal tube-type preheater was used to deliver the gas to the retorts at 400° C. (752° F.) and under optimum conditions it was possible to pyrolyze 70.8 cubic meters (2500 cubic feet) of gas per hour.

Later, this arrangement was modified by the use of steel connecting bends so that three retorts could be operated in series. The preheater temperature was raised to 650° C. (1202° F.). Furnace temperature was about 1200° C. (2192° F.). The results of this work are summarized in Table I.

METAL TUBES

The temperatures required for gas pyrolysis are high for tubes constructed of metal, and, on the large-scale development work, only certain special steels, costing 2 s. 6 d. to 3 s. 6 d. per pound, proved satisfactory. Many metals and alloys have been tested in the laboratory and on the plant and of these an alloy steel sold by Hadfields, Ltd., as H. R. 4 and containing 26 per cent chromium, 1.5 per cent manganese, 0.9 per cent silicon, 0.15 to 0.2 per cent carbon, and not more than 0.3 per cent nickel, was the best. Even this steel, after continued use with a skin temperature of 1000° to 1100° C. (1832° to 2012° F.) becomes brittle. After 3 months of continuous operation under these conditions there was no sign of corrosion, but the structure of the metal had definitely changed. In large-scale pyrolysis of natural gas, the petroleum chemist is ahead of the metallurgist and calls for his assistance in better heat-resisting metal.

Sir Robert Hadfield points out in his recent treatise on Special Steels that, while chromium is the chief agent in resisting oxidation in alloy steels at high temperatures, a high-nickel content gives greater stability to the metal under long continuous service. In other words, the high-chromium heat-resisting steel may be liable to grain growth and embrittlement while the nickel-chromium types retain their original structure.

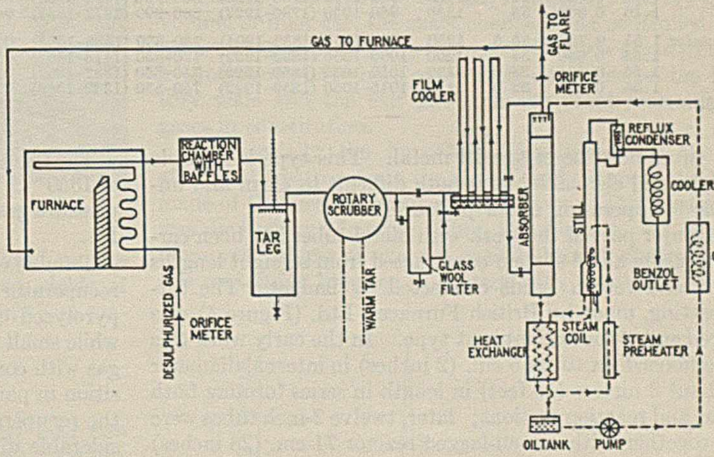


FIGURE 3. DIAGRAM OF PYROLYSIS PLANT

Steels with a higher percentage of nickel than that of the H. R. 4 metal used in Persia are now available.

It is of vital importance, in order to keep conditions as favorable as possible, that a high degree of turbulence should exist in the gas flow through the tubes. Heat transfer under these circumstances is satisfactory, and the limiting factor in the coil type of tube furnace becomes the pressure drop across the furnace. This points to small-bore tubes 5 and 10 cm. (2 and 4 inches) i. d., and in certain cases, cores, since it is found that a high surface to volume ratio is favorable to the formation of benzene. A method of avoiding small-bore tubes is by the use of a concentric-tube heating element. This consists of a nest of tubes arranged like a set of cork borers except that gas enters the small central tube and passes along the annulus between that tube and the next larger tube, and so on, finally coming out from the annulus formed by the largest and next largest tubes. This method of heating has two distinct advantages: (1) It is possible to obtain very high over-all heat transfer rates of the order of 6800 kg. cal. per square meter (25,000 B. t. u. per square foot) of external pipe exposed to the radiant furnace; (2) only the

TABLE I. PYROLYSIS OF NATURAL GASES USING FIRE CLAY RETORTS

Description of Retort	Preheat Temp.	Type of Gas	Av. Furnace Temp.	Steam Added	Sp. Gr. of Final Gas (Air = 1)	Yield of Crude Benzene Per cu. m. inlet gas	Yield of Crude Benzene Per 1000 cu. ft. inlet gas	Sp. Gr. and Quality of Crude Benzene	Throughput of Gas
	° C. (° F.)		° C. (° F.)	%		Liter	Imp. gal.		Cu. m. (cu. ft.)/hr.
15.24 cm. (6 in.) i. d., 3.81 cm. (1.5 in.) thick; 4 retorts in parallel	400 (752)	Stripped low-pressure gas H₂S reduced to 1–2%	1050 (1922)	5	0.6	0.104	0.65	0.870; (75% off below 150° C.)	10.9 (385) per retort
15.24 cm. i. d., 3.81 cm. thick; 3 retorts in series	650 (1202)	Unstripped low-pressure gas, partly desulfurized	1190–1210 (2174–2210)	5	0.60	0.176	1.1	0.829 (73% off below 150° C.)	33.7 (1190) per 3 retorts in series
	650 (1202)	Same as above	1190–1210 (2174–2210)	5	0.65	0.128	0.8	0.880 (79% off below 150° C.)	45.9 (1620) per 3 retorts in series
7.62 cm. (3 in.) i. d., 1.9 cm. (0.75 in.) thick; 4 retorts in series	650 (1202)	Unstripped low-pressure gas, H₂S–free	Exit temp. from reaction tube, 950 (1742)	Nil	0.65	0.189	1.18	0.869 (90% off below 175° C.)	31.2 (1100) per 4 retorts in series

TABLE II. PYROLYSIS OF DESULFURIZED NATURAL GASES USING SPECIAL METAL (H. R. 4) REACTION TUBES

Conditions of Operation							Benzene Production and Properties						
										Distillation			
Gas	Sp. Gr. of Gas	Sp. Gr. of Exit Gas	Throughput of N_2-Free Gas per Hour		Tube Skin Temp.	Av. Exit Gas Temp. from Reactor	Yield of Crude Benzene Per cu. m. gas	Per 1000 cu. ft. gas	Sp. Gr. of Crude Benzene	Distilling up to 175° C. (347° F.)	Benzene fraction, 70–90° C. (158–194° F.)	Toluene fraction 105–115° C. (221–239° F.)	Styrene and xylene fraction 130–145° C. (266–293° F.)
			Cu. m.	Cu. ft.	° C. (° F.)	° C. (° F.)	Liter	Gallons		%	%	%	%
Low-pressure stripped	1.06	0.700	49	1730	980–1060 (1796–1940)	800–900 (1472–1652)	0.153	0.95	0.886	72.3	47.8	6.4	4.8
	1.06	0.650	41	1450	980–1060 (1796–1940)	800–900 (1472–1652)	0.184	1.14	0.888	83.5	62.25	6.1	6.1
	1.06	0.625	38	1350	990–1050 (1814–1922)	800–900 (1472–1652)	0.169	1.05	0.888	89.1	74.0	4.6	4.1
	1.06	0.600	34	1300	1010–1055 (1850–1931)	800–900 (1472–1652)	0.155	0.96	0.886	90.4	73.4	5.3	5.8
	1.06	0.575	35.5	1250	1010–1055 (1850–1931)	800–900 (1472–1652)	0.145	0.90	0.886	90.3	75.3	4.1	5.6
Low-pressure unstripped	1.16	0.700	52.5	1850	980–1060 (1796–1940)	800–900 (1472–1652)	0.195	1.21	0.866	88.5	57.6	14.7	7.1
	1.16	0.650	47	1650	980–1050 (1796–1922)	800–900 (1472–1652)	0.234	1.45	0.890	87.5	61.1	8.8	7.5
	1.16	0.625	41	1450	980–1050 (1796–1922)	800–900 (1472–1652)	0.244	1.51	0.888	85.1	65.2	7.7	6.9
	1.16	0.600	38	1350	980–1050 (1796–1922)	800–900 (1472–1652)	0.236	1.46	0.889	91.7	69.1	6.4	7.1
Accumulator	1.55	0.700	35.5	1250	1000–1040 (1832–1904)	750–850 (1382–1562)	0.355	2.2	0.886	82.1	55.8	7.9	7.4
	1.55	0.650	34	1200	1000–1050 (1832–1922)	770–850 (1418–1562)	0.403	2.5	0.883	85.1	63.8	8.4	6.5
	1.55	0.625	33.5	1190	1010–1050 (1850–1922)	750–850 (1382–1562)	0.42	2.6	0.892	87.0	70.0	5.5	5.6
	1.55	0.610	32.5	1150	1015–1050 (1859–1922)	750–850 (1382–1562)	0.29	1.8	...	..	..	..	...

larger tubes need be of special metal. This type is suitable for cast-metal elements but is both difficult to clean and unsuitable for operation under pressure.

The major part of the work with metal tubes has been carried out using a coil system constructed from straight lengths of tube and return bends connected by flanges. The furnace setting, made by British Furnaces, Ltd. (Figure 4) was gas-fired and of the radiant heat type. In the early work this setting housed six tubes 5 cm. (2 inches) in internal diameter and about 3 meters (10 feet) in length in series forming both preheat and reaction sections; later, twelve 2-inch tubes were used, together with a well-lagged reactor 71 cm. (28 inches) in internal diameter and 96 cm. (38 inches) long. Tests were also carried out in this furnace using 10.2-cm. (4-inch) i. d. tubes.

Calorized tubes were tested and had an apparent life of 2 to 3 weeks under operating conditions; tubes of an alloy steel containing 20 per cent chromium, 9 per cent nickel, and 0.2 per cent carbon made by Hadfields, Ltd., and designated "C. R. 2" appeared to have a life of 4 to 6 weeks. Attention was later concentrated on the use of H. R. 4 steel in the hottest zone. Using this heat-resisting steel, a full series of experiments was carried out with the various gases; the results are summarized in Table II. This shows that the optimum conversions to crude benzene of stripped gas, unstripped gas, and accumulator gas are 0.184, 0.244, and 0.42 liter per cubic meter (1.14, 1.51, and 2.6 gallons per 1000 cubic feet), respectively. The figure of 0.244 compares favorably with 0.189 liter per cubic meter (1.18 gallons per 1000 cubic feet) from the same gas using fire clay retorts.

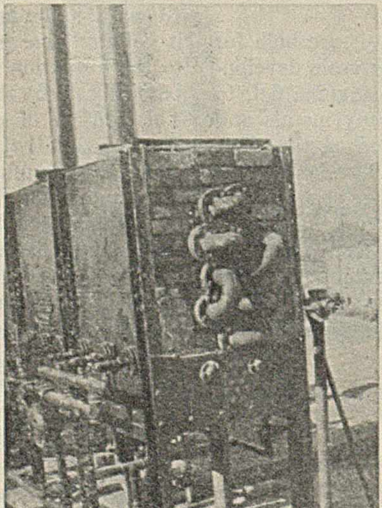


FIGURE 4. "BRITISH FURNACES, LTD., FURNACE" USED IN PERSIA

Twelve 2-inch internal diameter metal tubes are arranged in series; the lagging box has been removed from the return bends.

RECUPERATOR FURNACE

An attempt was made to produce benzene in a recuperator type of furnace incorporating fire clay, silicon carbide, and silicon blocks. Heating of the gas was by flue gases passing between the blocks.

With this recuperative furnace a separate tubular preheater section was used, constructed of Green cast-iron elements in which the gas was heated to 600° C. (1112° F.) before entering the recuperator.

The throughput of this furnace using a fire box temperature of 1350° C. (2462° F) was 10,000 cubic feet per hour of high-pressure gas giving an exit gas temperature of 850° C. (1562° F.).

Trouble was encountered in the form of leakage between the recuperator blocks. Any positive pressure on the gas to be pyrolyzed caused gas to leak through and burn in the flues, while small negative pressures led to the dilution of pyrolyzed gas with considerable quantities of flue gases. Carbon deposition in parts of the system was sufficiently serious to choke the recuperator elements, and cleaning was a matter of considerable difficulty.

The average yield of crude benzene was 0.161 liter per cubic meter (1 gallon per 1000 cubic feet) of hydrogen sulfide-free stripped gas with a maximum of 0.197 liter per cubic meter (1.23 gallons).

In the type of furnace used, recuperator blocks must be ruled out for commercial operation on the ground of fragility, low heat transfer, and the difficulty of making the joints between the blocks gas-tight at high temperatures.

SURFACE COMBUSTION AND SUBMERGED FLAME HEATING

These methods of heating gas for pyrolysis were tried out using several designs of furnace setting and heaters (Figure 5). Apart from the necessity of handling greater quantities of gas and the greater residual quantity of benzene left in the gas after stripping, there appears to be little objection to the dilution of pyrolyzed gases with flue gases. This leads to the possibility of using flue gases as a direct means of heating the gas to be pyrolyzed with the elimination of the use of expensive-resisting metal tubes.

In every case it was found that on the grounds of both benzene yield per 1000 cubic feet of gas and quality of benzene produced, these methods are considerably inferior to the metal tube heaters. Furthermore, in surface combustion, heater trouble was met owing to back-firing.

OTHER METHODS OF HEATING

A regenerative type of furnace was tried out for pyrolysis work on a semi-commercial scale with some success, but the tests were not sufficiently extensive to come to a final conclusion.

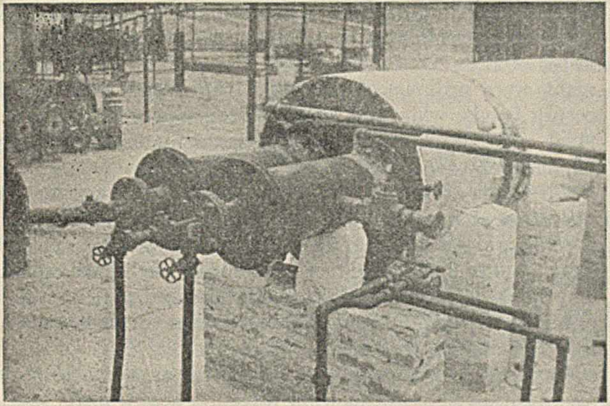


Figure 5. Surface Combustion Furnace in Persia

Silicon carbide blocks and tubes have been used on the plant, but for several reasons, including reduced yields of benzene and porosity under operating conditions, these materials were not highly successful.

Products

Liquid products may be conveniently divided into two products: (1) boiling from 0° to 200° C. (32° to 392° F.) and (2) boiling 200° C. and over.

Fraction Boiling from 0° to 200° C. The Engler distillation figures for such a product are:

Sp. gr. of crude spirit (cutting roughly at 200–210° C.) at 60° F. (15.6° C.)	0.892
Initial boiling point, ° C.	45
Distillate to 50° C., %	Few drops
75	12
100	75
125	80
150	85
175	88
200	91
Total, %	93
Residue, %	4
Loss, %	3

If the crude gasoline fraction is distilled through an efficient column packed with Lessing rings, the results obtained may be set out as in Figure 6. This method of drawing the distillation curve indicates four peaks at about 80°, 110°, 140°, and 180° C.

The large fraction, boiling around 80° C. and representing, in the range 70° to 90° C., up to 75 per cent of the gasoline boiling below 200° C. was mainly benzene, although in the region 70° to 77° C. unsaturation was observed. The unsaturation may be due to the presence of a constant-boiling mixture. It is of interest that the presence of cyclohexene has been established in this fraction.

From the fraction 105° to 115° C. pure toluene was isolated and was shown to be the predominating constituent.

The bulk of the fraction 135° to 150° C. was shown to be styrene and in quantity this hydrocarbon represented about 4 per cent of the gasoline up to 200° C. Beside the styrene in this fraction, *m*- and *p*-xylenes were present.

From the fraction around 180° C. indene was isolated and identified.

Tar. In the tar fraction has been included products boiling above 200° C. (392° F.). From this fraction naphthalene, anthracene, and phenanthrene were readily isolated and identified, and the presence of chrysene was indicated.

Attempts were made to determine the naphthalene content of the pyrolyzed gases since this compound is troublesome in large-scale operation, and it has been stated that 10 grains of naphthalene will block a 0.5-inch pipe for a length of about one foot. Using picric acid solution, 0.23 pound per 1000 cubic feet was obtained before the gas had passed through the tar leg.

In plant operation most of the tar was removed in the coolers, but the remainder was carried forward as a fog and was removed by glass-wool filters or by electrical deposition. The normal make of tar was about 4 pounds per 1000 cubic feet of gas.

Gas. In the pyrolysis operation, for production of aromatics, the volume of exit gas is normally about twice the volume of inlet gas, the exact change being controlled by the nature of the gas to be pyrolyzed. The exit gases from pure hydrocarbons have been extensively examined on the laboratory scale and the exit gases on the plant resemble these gases in constitution.

Commercially the important constituents of the gases after heat treatment are the olefins, and determinations were made of the olefin content of these gases. The method used was devised by Manning, King, and Sinnatt. In outline, a measured volume of gas was passed through absorption vessels containing bromine in contact with water, the bromides were purified and fractionated, the unsaturated hydrocarbons regenerated by use of zinc-copper couple, and finally the gas so obtained was analyzed by a special method on the Bone and Wheeler gas analysis apparatus.

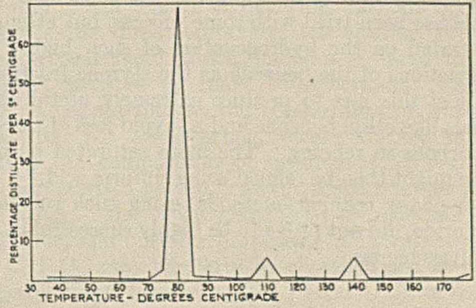


Figure 6. Distillation of Crude Benzene Fraction up to 200° C.

With a gas equivalent to accumulator gas, the increase in volume due to pyrolysis was such that 1 volume of inlet gas gave 2.5 volumes of exit gas. When this was taken into account the results of the analysis were:

	Exit Gas (N_2-Free) %	Inlet Gas (H_2S- and N_2-Free) %
Total unsatd. hydrocarbons	20.0	50.0
Ethylene	18.0	45.0
Propylene	0.96	2.4
Butylene	0.51	1.27
Butadiene	0.43	1.08
Unaccounted for	0.10	0.28

Here, after benzene production, is a gas containing 20 per cent olefins, essentially ethylene, representing a 50 per cent volume conversion on the ingoing gas. This exit gas is a potential source of further liquid hydrocarbons or alternatively other products such as alcohols, ketones, etc.

Carbon

The deposition of some carbon appears to be inevitable in pyrolysis operations for the production of benzene. Certain materials inhibit the production of carbon and, when used under suitable conditions, carbon deposition in the reaction plant may become almost negligible. Cleaning, when necessary, may be accomplished by air-blowing after the hydrocarbon atmosphere has been replaced by an inert one.

Refining of Benzene

Benzene derived from the pyrolysis of natural gas appears to differ from coal-tar benzene only in the relative proportions of its constituents, and the same general methods of refining are applicable in both cases. Where the product of pyrolysis is intended as a blending stock, the following are some of the methods of treatment available: inhibitors, sulfuric acid treatment, hydrogenation, fractionation and the separate treatment of the fraction, and vapor-phase refining.

Bound up with this question of refining is also the maximum permissible sulfur content of the benzene. The normal product using metal tubes contained 0.5 per cent sulfur, and this, for blending purposes, was considered satisfactory.

Pyrolysis benzene is a very suitable material for the testing of inhibitors, and considerable success can be expected by this method.

Sulfuric acid refining has proved satisfactory, in that the product, after treatment, is stable and of good quality, but this method is wasteful of what may be useful unsaturated material. Details need not be given as these follow the normal refining lines.

Hydrogenation may be applied to the benzene as a whole, and this has been tried with some success, but attention was concentrated on the hydrogenation of such highly unsaturated fractions of the benzene as the styrene fraction. The purpose of this was to produce extremely useful antiknock materials like ethyl benzene and so avoid loss of unsaturated hydrocarbons in refining. The more saturated parts of the benzene might then be refined using sulfuric acid.

Vapor-phase refining methods, using such substances as zinc chloride, did not prove to be highly successful in the case of pyrolysis benzene.

Influence of Pressure on Pyrolysis of Hydrocarbons

Large-Scale Pyrolysis of Natural Gas. On the semitechnical scale, tests were carried out using metal tubes in the furnace section at a pressure of 30 pounds per square inch gage. This, unfortunately, was a limiting pressure owing to the construction of the plant. The heating system consisted of 12 × 2 inch i. d. tubes in series, of which the first eight were ordinary 2-inch steel tubes and corresponding return bends, while the four hottest tubes were of H. R. 4. steel with return bends of the same material. A lagged expansion box was used.

Operation at 30 pounds per square inch was compared with operation at 6 pounds per square inch using stripped gas of specific gravity 1.00 to 1.01. The throughput was increased from 1800 to 2800 cubic feet per hour at the higher pressure. The benzene production was little changed and was of the order of 1.1 gallon per 1000 cubic feet of nitrogen- and hydrogen sulfide–free gas.

Under 30 pounds per square inch pressure the plant was easier to run than at the lower pressure, heat transfer was improved, throughput increased, and yield remained the same.

ACKNOWLEDGMENT

Acknowledgment is due the Anglo-Persian Oil Company, Ltd., for making this semiworks-scale investigation possible and for granting permission to publish the results.

To R. V. Wheeler, J. F. Thorpe, J. Jameson, G. H. Coxon, A. E Dunston, and F. B. Thole appreciation and thanks are due for criticism and valuable suggestions as the work proceeded.

The writer wishes to acknowledge his indebtedness to E. N. Hague for assistance in preparing Part II for publication, and also for the identification of the various hydrocarbons present in the crude benzene.

Received September 7, 1933.

Thermal Decomposition of the "Coal Hydrocarbon"

H. H. Lowry, Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

COAL is not a hydrocarbon. Even if we leave out of consideration the technically very important constituents ash, moisture, sulfur, and nitrogen, the data in Table I show that, in a high-rank bituminous coal, there may be one to nine oxygen atoms to every hundred atoms comprising the coal substance. Only in the anthracites, which are not of commercial interest from the viewpoint of use in any process of recovering by-products from thermal decomposition, do we approach a substance having the composition of a hydrocarbon. An attempt will be made later to show that a study of the thermal decomposition of anthracite may lead to a clearer understanding of the nature of the solid residue obtained in all normal destructive distillations of solid organic complexes.

Table I. Chemical Composition of Coals

(In atomic per cent[a])

Coal	C	H	O
Peat	38±3	45±3	16±3
Lignite	47±4	41±4	12±2
Bituminous	56±8	39±5	5±4
Anthracite	78±12	20±12	1±1

[a] Calculated on the basis % C + % H + % O = 100. For each 100 atoms of C, H, and O, bituminous coals normally contain 1 to 2 atoms of N and 0.3 to 3 atoms of S.

Free hydrocarbons exist in coal in only relatively insignificant amounts, if at all. That certain solvents may extract hydrocarbons from coal at temperatures from 80° to 260° C.—temperatures below active gaseous decomposition of coal—is frequently cited as evidence to the contrary. This argument appears to be insufficient. A substance dissolves in a solvent owing to the fact that its partial pressure in the solvent is less than its normal vapor pressure—in this respect solvent extraction is analogous to distillation. The fact that solvents extract materials from coal at lower temperatures than are effective in distillation does not necessarily signify their prior existence as such in the coal. For distillation a vapor-pressure gradient of an entirely different order of magnitude is necessary than for solvent extraction. In this connection consider, for example, sugar which may be distilled only at extremely low pressures (*20*) but may dissolve readily in the appropriate solvent. Also, it is clear that thermal decomposition in the presence of a solvent is easier than in a vacuum (or at atmospheric pressure). Elementary electrostatics states that the attraction between two oppositely charged bodies is less the higher the dielectric constant of the medium in which the bodies exist. Referring specifically to coal, the presence of a solvent therefore loosens the entire solid structure in such a way that less kinetic energy in the form of heat is necessary to cause rupture of the bonds holding the solid together than in the absence of the solvent. This explanation accounts for the greater effectiveness of pyridine (dielectric constant 9.4) than of benzene (dielectric constant 2.1) as a solvent for coal at their normal boiling points, completely ignoring specific chemical reactions. Although coal is an organic solid showing macro- and microscopic heterogeneity, any attempt to distinguish between "chemical" bonds holding atoms together in a molecule and "physical" bonds holding atoms together between neighboring molecules seems academic and of no real value. It appears reasonable, therefore, to consider solvent extraction as a means for studying the mildest type of thermal decomposition.

Evidence is presented to show that coals from the peat stage through the higher ranks contain as an essential part of their structure six-membered carbon rings similar to those present in aromatic compounds and graphite. Coal is not a hydrocarbon and contains little, if any, free hydrocarbon. Consideration of the nature of the products obtained from coal with increasing severity of thermal treatment suggests that the aromatics found in coal tar result primarily from dehydrogenation and decarboxylation of depolymerized nuclei present in the original coal. Finally data are presented which support the idea that "free" carbon in pitch, coke, and charcoal may be regarded as highly polymerized aromatic hydrocarbons which gradually and regularly approach graphite as the temperature at which they are formed increases.

CONSTITUTION AND FORMATION OF COAL

If coal is neither a hydrocarbon nor contains free hydrocarbons, how can the presence of a large proportion of aromatic hydrocarbons in coal tars be explained? A consideration of the chemical constitution and the mode of formation of coal offers an explanation. Since Hawley and Harris (*6*) have shown that the aromatic compound, lignin, may be prepared from the aliphatic compound, cellulose, we need not concern ourselves with which of the two is the mother substance of coal. Furthermore, Schrauth (*17*) has shown that the products obtained by Willstätter and Kalb (*21*) from the reduction of lignin, cellulose, and sugars may all be regarded as derivatives of the aromatic nucleus shown in Figure 1*A*. Schrauth postulates the formation of coal as a result of condensation and polymerization of compounds containing this same nucleus, as shown in Figure 1*B*. In this case, coal may be regarded as having as an essential element of structure the six-carbon ring characteristic of aromatic hydrocarbons and their derivatives. This conclusion is supported by two other independent modes of reasoning.

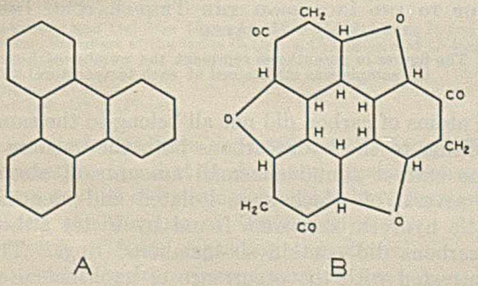


FIGURE 1

A. Hydrocarbon skeleton found by Schrauth (*17*) in the products obtained by Willstätter and Kalb (*21*) by the reduction of lignin, cellulose, and sugars.
B. Derivative of *A* suggested by Schrauth as the parent substance of coal.

In peat, the earliest recognized form of coal, alkali-soluble acids, called "humic" acids, have long been known to exist. During coalification these acids condense and lose their solubility in alkali but may be regenerated by mild oxidation (cf. citation *5*). Humic acids may therefore be regarded as an important step in the formation of coal. Fuchs (*4*) has concluded that humic acids are condensation products of a compound having the aromatic structure shown in Figure 2. The free peripheral bonds may hold hydrogen atoms, hydroxyl, methoxy, or carboxyl groups which provide the means for condensation.

The essential aromatic nature of the coal substance is further indicated by the work of Bone, Horton, and Ward (*3*) who obtained as high as 49 per cent yields of benzene carboxylic acids by oxidation of coals of various ranks by alkaline permanganate at 100° C.

Evidence has been presented to show that coals from the peat stage through the higher ranks are aromatic in structure. Keeping this in mind and considering that the agencies effective in coalification are commonly regarded to be heat and pressure, the data presented in Figure 3 may help to make clear the changes undergone in the metamorphosis of coal and in its thermal decomposition. On Figure 3, showing carbon, hydrogen, and oxygen as its three coördinates (cf. citation *15*), there is plotted a coal band which includes a large majority of published analyses of coals. Furthermore, there are two lines: One, starting at the composition of water and ending at 100 per cent carbon, passes through a point representing the composition of cellulose ($(C_6H_{10}O_5)n$), and may be characterized as the "carbohydrate line" or a "line of dehydration;" the other, starting at the composition of carbon dioxide, and only for purposes of illustration passing through $C_6H_{10}O_5$, may similarly be characterized as a "line of decarboxylation" (loss of carbon dioxide). The coals all lie between these lines, and it may be concluded that the first effect of heat and pressure on the vegetable matter, from which the coals are formed, is the elimination of carbon dioxide and water, primarily the latter. Only when we reach the higher rank coals does another agency appear; we may infer that to form these higher rank coals more heat and pressure are required than for the lower rank coals, and that sufficient methane is lost during the later changes in rank to cause the observed change in curvature of the coal band. The loss in methane may be attributed directly to the higher temperatures involved. Figure 3 indicates the modification in these conclusions necessitated if one postulates the loss of carbon monoxide, ethane, or other hydrocarbons. It is of interest to note that, if decarboxylation of cellulose could be accomplished with relatively little dehydration, the result would be a hydrocarbon, possibly similar to petroleum. Treatment of cellulose in water (which would retard dehydration) containing high concentrations of alkali, favoring decarboxylation, has actually been shown by Berl (*2*) to yield an "artificial petroleum;" in weaker alkali (less decarboxylation) the product resembled coal. Both facts would be expected from consideration of Figure 3.

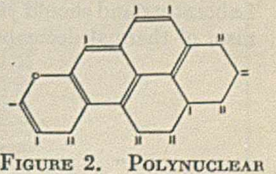


FIGURE 2. POLYNUCLEAR AROMATIC SKELETON OF A UNIT OF STRUCTURE OF HUMIC ACID AS SUGGESTED BY FUCHS (*4*)

The indicated free bonds contain hydrogen, hydroxyl, methoxyl, and carboxyl groups.

Throughout the greater part of the slow process of coalification, the progressive change in composition yields coals approaching more nearly to hydrocarbons, as is also shown by

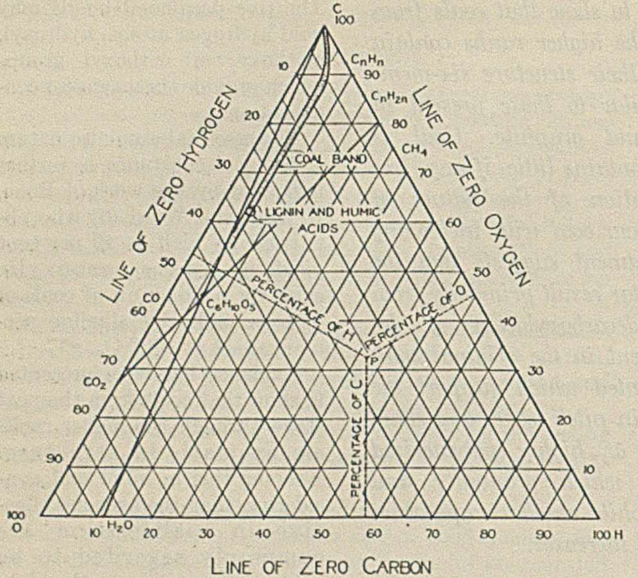


FIGURE 3. DIAGRAMMATIC REPRESENTATION OF COMPOUNDS OF CARBON, HYDROGEN, AND OXYGEN, INCLUDING THE "COAL BAND"

the data in Table I. It is to be expected that, in the more rapid processes represented by laboratory pyrolyses, the simple picture graphically shown in Figure 3 is not applicable. In addition to the changes taking place in coalification, under usual conditions of carbonization a more deep-seated breakdown of the condensed and polymerized aromatic coal substance occurs, and, since the distillate is free to escape and condense, coal tar results. The complexity of the units resulting from the pyrolysis depends entirely on the severity of the thermal treatment. Benzene and its homologs are to be found only in high-temperature tar and do not represent the initial products of thermal decomposition of coal. Solvent extraction, vacuum distillation, and low-temperature carbonization represent increasing severity of thermal treatment of coal and yield progressively simpler products, all, however, more complex than the "secondary" products in high-temperature tar. No one has yet treated a single coal by all these methods and compared the products quantitatively. This is one of the objectives of the Coal Research Laboratory and should yield information on the actual mechanism of thermal decomposition of coal.

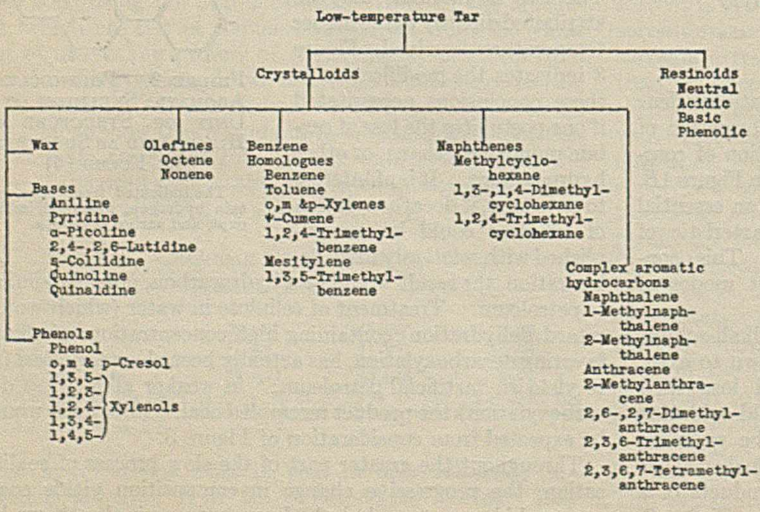


FIGURE 4. CONSTITUENTS OF LOW-TEMPERATURE TAR (*12*)

THERMAL DECOMPOSITION OF COAL

Data are, however, available in the literature that throw much interesting light on this question. Pictet (*13*) has made a very comprehensive study of the benzene extract obtained from coal at 80° C. and a vacuum tar obtained at 450° C. and 15 to 20 mm. pressure. The coal used in the solvent extraction was a high-volatile bituminous coal from the Saar, while that used in the distillation study was a coal of similar rank, Montrambert. 5200 kg. of coal, on extraction for 4.5 days in two portions, yielded a total of 13.30 kg. of extract. Vacuum distillation of 1500 kg. of coal provided 60 kg. of tar. Both the tar and the extract were subjected to detailed separation and many individual chemical compounds were identified. In Table II is given a partial list of hydrocarbons isolated together with compounds of the same series identified by Mabery (*11*) in crude petroleums. In many cases the structure of the hydrocarbons was identified, and the hydrocarbons containing more than eleven atoms of carbon did not all belong to the same series. In addition to the hydrocarbons both the vacuum tar and benzene extract contained small amounts of alcohols and bases, several of which were isolated and identified. No aromatic hydrocarbons were found by Pictet although the hydrocarbons did contain six-membered rings. This is to be contrasted with the occurrence of naphthalene reported by several investigators in petroleum (*19*). It seems reasonable to assume that the aromatic hydrocarbons in coal tar have been formed by dehydrogenation of hydrocarbons similar to those listed in Table II as well as by further pyrolysis of the coal substance itself at higher temperatures. Sufficient evidence is not available to state definitely that aromatic hydrocarbons may not be formed by "primary" thermal decomposition of coal.

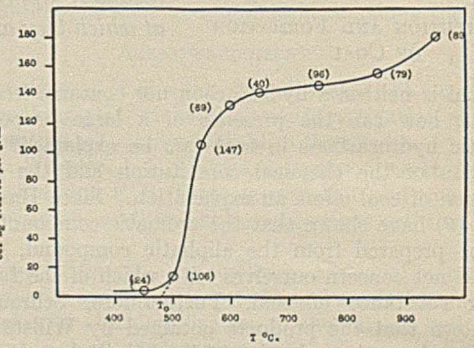


FIGURE 5. TOTAL CUBIC CENTIMETERS OF HYDROGEN EVOLVED PER GRAM OF ANTHRACITE COAL, UP TO AND INCLUDING THE TEMPERATURE INDICATED

The figures in parentheses represent the number of hours the sample was maintained at each temperature.

A comparison of the data reported by Pictet on the composition of vacuum tar obtained at a temperature not exceeding 450° C. with similar data on low-temperature tar indicates that aromatic hydrocarbons appear first between 450° and 600° C. The most thorough published work on identification of the chemical compounds in low-temperature tar has been presented by Morgan and collaborators working in coöperation with the Fuel Research Board in Great Britain. His results are conveniently summarized in part in Figure 4 (*12*). These data indicate clearly that temperatures of 1000° C., characteristic of usual methods of coal carbonization, are not essential to the formation of the aromatic compounds found in high-temperature tar. It is true that high-temperature tar does contain a larger proportion of the simpler aromatics of the benzene series than does low-temperature tar, but this would be expected from cracking of the more complex aromatics.

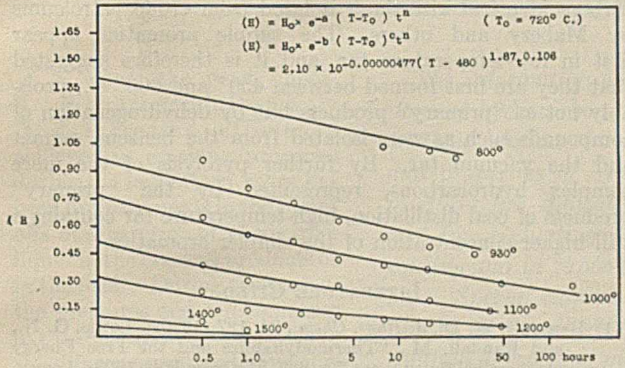


FIGURE 6. PERCENTAGE HYDROGEN BY WEIGHT IN THE SOLID RESIDUE OF AN ANTHRACITE COAL HEATED TO DIFFERENT TEMPERATURES AS A FUNCTION OF TIME

Circles represent observed points; curves are calculated from the equation given in Table III, footnote *a*.

TABLE II. HYDROCARBONS ISOLATED FROM VACUUM TAR AND BENZENE EXTRACT OF COAL (*13*) AND FROM PETROLEUM (*11*)

SATURATED	UNSATURATED[a]	SATURATED	UNSATURATED[a]	SATURATED	UNSATURATED[a]
....	C_7H_{10}[b]	$C_{13}H_{24}$[b,c,d]	$C_{12}H_{16}$[c]	....	$C_{14}H_{16}$[b]
C_8H_{16}(?)[b]	C_8H_{12}[b,c]	....	$C_{12}H_{14}$[c]	$C_{16}H_{22}$[d]	$C_{16}H_{30}$[e]
C_9H_{18}(?)[b,d]	C_9H_{14}[b,c]	$C_{13}H_{26}$[b,c,d]	$C_{13}H_{16}$[b,c]	....	$C_{17}H_{20}$
$C_{10}H_{20}$[b,c,d]	$C_{10}H_{16}$[b,c]	...	$C_{13}H_{12}$[b]	$C_{30}H_{60}$[b,c,e]	....
$C_{11}H_{22}$[b,c,d]	$C_{11}H_{16}$[b,c]				

[a] Markovnikov and Ogloblin [*Ber.*, **16**, 1873 (1883)] have found in Russian petroleum, members of the series C_nH_{2n-8}, C_nH_{2n-10}, and C_nH_{2n-12}.

[b] Benzene extract.

[c] Vacuum tar.

[d] Petroleum.

[e] Galician petroleum (Pictet).

So much work has been reported on the composition of high-temperature tar that it does not appear necessary to present here any list of hydrocarbons that have been isolated. It has been the purpose of the paper thus far to present evidence regarding the source of the aromatic hydrocarbons found in coal tar although coal itself is not a hydrocarbon and contains little, if any, free hydrocarbon. According to the point of view presented, this source is to be found in the chemical structure of the coal itself in which several investigations have clearly shown the existence of polynuclear aromatic structures.

Such data as have been cited on the composition of benzene extract, vacuum tar, and low-temperature tar are necessarily limited in their application to coals of ranks lower than anthracite. According to the figures presented in Table I, anthracite of all the coals approaches most nearly to a hydrocarbon in composition. In the progressive metamorphism of coal, with the elimination of water, carbon dioxide, and methane, it seems unreasonable to expect that the aromatic structure characteristic of coals of lower rank would disappear during the transition to anthracite, which therefore may be regarded as a highly condensed multinuclear aromatic hydrocarbon. This point of view is supported by x-ray evidence (*8*), which has proved the existence in anthracite of carbon atoms arranged in six-membered rings as in both benzene and in graphite.

THERMAL DECOMPOSITION OF ANTHRACITE

A study of the thermal decomposition of anthracite yields information on the nature of the more condensed hydrocarbons, among which we may include the "free" carbon in pitch, coke, and charcoal (cf. citation *1*). When anthracite is pyrolyzed, it behaves similarly to other complex molecules which contain the remarkably stable six-carbon ring structure, losing hydrogen and the simpler hydrocarbons (predominately methane) and leading to chemical condensation through carbon-to-carbon linkage. In this way larger and larger molecules are formed (cf. citation *7*), richer in carbon and poorer in hydrogen until the end stage, graphite, is reached. For each anthracite coal there appears to be a critical temperature (T_0) which must be exceeded before evolution of hydrogen begins. Above this temperature the elimination of hydrogen progresses slowly and regularly as shown in Figure 5 (*10*). The composition of the residue is a function of both the maximum temperature to which the sample is heated and the time at this temperature, the former being more important as is evident from Figure 6. (The percentage figures shown are on a weight basis; to change to an atomic basis it is necessary to multiply the percentage hydrogen by 10–11.) With different coals, the results of analyses (for method of analysis, see original paper, *10*), for carbon and hydrogen can be equally well expressed by suitable modifications of the values of the constants in the equation shown on Figure 6. Similar data are given for fourteen coals in Figure 7 (*10*), each point representing the average of multiplicate analyses of samples heated to the indicated temperature ± 5° C. for 30 minutes in an atmosphere of hydrogen. For purposes of comparison, there are plotted also in Figure 7 two points, *V*, for wood charcoal (*18*), a point, *R*, for activated coconut charcoal (*16*), and a point, *P*, for sugar charcoal (*14*).

It is of particular interest that the activated charcoal falls within the band of the coal residues, since "active" carbons have been frequently regarded to be a special form of carbon. The process of activation consists essentially in heating the carbonaceous residue from thermal decomposition of anthra-

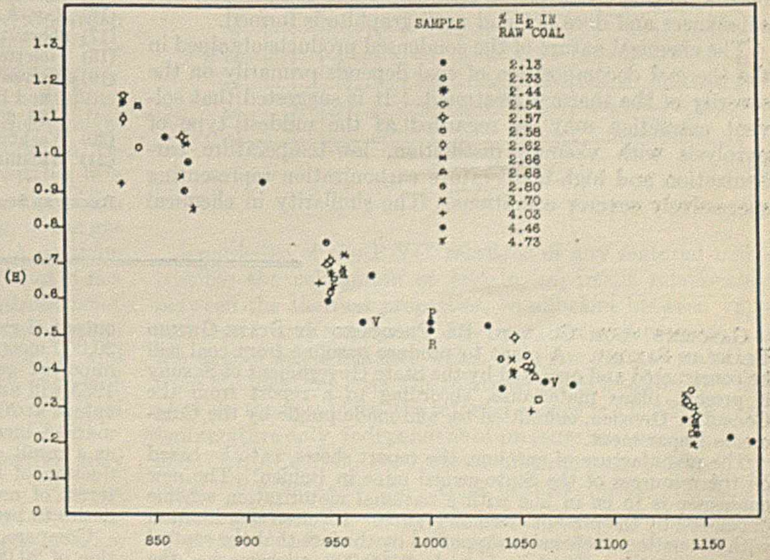


FIGURE 7. HYDROGEN CONTENT DATA OF FOURTEEN DIFFERENT COALS HEATED IN AN ATMOSPHERE OF HYDROGEN FOR 30 MINUTES AT VARIOUS TEMPERATURES

cite, nutshells, wood, or sugar in an atmosphere of steam or carbon dioxide. The data in Table III (*10*) show that the carbon to hydrogen ratio is essentially independent of the atmosphere in which the samples are heated. This has elsewhere (*9*) been interpreted as support of a hypothesis that for each given carbon to hydrogen ratio there is a specific adsorptive capacity characteristic of a definite degree of unsaturation of the solid and that the activation process is primarily one of increasing the surface by chemical action. As the residues are heated to progressively higher temperatures, they approach more and more closely to graphite in properties, the crystal size as indicated by x-ray studies increases (*8*), and the last traces of hydrogen are not eliminated until the carbon atoms have sufficient mobility to take the most stable configuration of graphite. In accordance with this point of view, "amorphous" carbons are complex hydrocarbons of aromatic structure and represent a definite stage in the thermal decomposition of any organic complex which leaves a solid residue on pyrolysis.

TABLE III. HYDROGEN CONTENT OF SAMPLES OF ANTHRACITE COAL TREATED AT DIFFERENT TEMPERATURES IN HYDROGEN, AIR, AND CARBON DIOXIDE (*10*)

TEMP. ° *C.*	H_2	AIR	CO_2	CALCD.[a]
900	0.76 (4)[b]	0.67 (9)	0.67 (6)	0.78
1000	0.49 (4)	0.48 (5)	0.47 (3)	0.49
1050	0.33 (1)	0.36 (3)	0.36 (3)	0.37
1100	0.29 (2)	0.28 (3)	0.28 (6)	0.28
1150	0.22 (7)	0.22 (1)	0.22 (8)	0.21
1200	0.20 (2)	0.18 (3)	0.17 (15)	0.15
1250	0.13 (1)	0.13 (2)	0.14 (1)	0.11
1300	0.10 (2)	0.09 (1)	0.09 (2)	0.08

[a] These samples were calculated using the following equation:

$$H = 2.10 \times 10^{-0.00000527\,(T-480)^{1.87}}$$

assuming $t^{0.106}$ = constant = 1.105, which is combined with the constant, a, giving the value 5.27×10^{-6}.

[b] The figures in parentheses are the number of samples prepared at the conditions indicated. The hydrogen content given is an average of this number.

SUMMARY

Coal is not a hydrocarbon and contains little, if any, "free" hydrocarbon. It contains, however, as an essential part of its chemical composition, the six-membered carbon ring structure characteristic of aromatic hydrocarbons. This nuclear structure becomes more and more condensed as coal passes through its various ranks, peat, lignite, bituminous coal, and anthracite. The condensation of aromatic nuclei appears to be the main reaction in the solid residue during pyrolysis of coal and other complex organic substances and does not end until graphite is formed.

The chemical nature of the condensed products obtained in the thermal decomposition of coal depends primarily on the severity of the thermal treatment. It is suggested that solvent extraction may be regarded as the mildest type of pyrolysis with vacuum distillation, low-temperature carbonization and high-temperature carbonization representing successively severer conditions. The similarity in chemical composition of a benzene extract and a vacuum tar obtained by Pictet was pointed out. Neither the extract nor the vacuum tar contained simple aromatic hydrocarbons, though both contained saturated and unsaturated hydrocarbons having six-carbon ring structures and both contained hydrocarbons identical with those isolated from crude petroleums by Mabery and others. The simple aromatics appear first in low-temperature tar, and it is therefore suggested that they are first formed between 450° and 600° C., probably not as "primary" products but by dehydrogenation of compounds such as were isolated from the benzene extract and the vacuum tar. By further pyrolysis of the more complex hydrocarbons, represented by the "primary" products of coal distillation, high-temperature tar contains a still higher concentration of the simpler aromatics.

LITERATURE CITED

(1) Bancroft, W. D., *J. Phys. Chem.*, 24, 127 (1920); Lewis, G. N., and Randall, M., "Thermodynamics and the Free Energy of Chemical Substances," p. 569, McGraw-Hill, 1923; Lowry, H. H., *J. Am. Chem. Soc.*, 46, 824 (1924); Brooks, IND. ENG. CHEM., 18, 521 (1926).
(2) Berl, E., *Z. angew. Chem.*, 43, 1018 (1930); *Proc. 3rd Intern. Conf. Bituminous Coal*, 2, 820 (1931); *Ann.*, 493, 97 (1932), 496, 283 (1932); *J. Inst. Fuel*, 5, 382 (1932).
(3) Bone, W. A., Horton, L., and Ward, A., *Proc. Roy. Soc.* (London), 127A, 480 (1930).
(4) Fuchs, W., *Brennstoff-Chem.*, 12, 266 (1931).
(5) Fuchs, W., "Die Chemie der Kohle," p. 471 et seq., Springer, 1931.
(6) Hawley, L. F., and Harris, E. E., IND. ENG. CHEM., 24, 873 (1932).
(7) Hurd, C. D., "Pyrolysis of Carbon Compounds," pp. 15, 93, A. C. S. Monograph No. 50, Chemical Catalog, 1929; Haber, F., *Ber.*, 29, 2691 (1896).
(8) Koch-Holm, Else, *Wiss. Veröffentlich. Siemens-Konzern*, 6, 188 (1927); Asahara, G., *Japan J. Chem.*, 1, 35 (1922); Hofmann, K. A., and U., *Ber.*, 59, 157 (1926); Hofmann, U., *Ibid.*, 61, 1180 (1928).
(9) Lowry, H. H., *J. Am. Chem. Soc.*, 46, 824 (1924); *J. Phys. Chem.*, 34, 63 (1930).
(10) Lowry, H. H., *Ibid.*, 33, 1332 (1929).
(11) Mabery, G. F., *Am. Chem. J.*, 19, 374, 419, 796 (1897); 25, 253 (1901); 33, 251 (1905).
(12) Morgan, G. T., *J. Soc. Chem. Ind.*, 51, 67T (1932).
(13) Pictet, A., *Ann. chim.*, [9] 10, 249 (1918); *Ber.*, 44, 2486 (1911), 46, 3342 (1913), 48, 926 (1915); *Chem.-Ztg.*, 40, 211 (1916); *Compt. rend.*, 163, 358 (1916), 165, 113 (1917); *Helv. Chim. Acta*, 6, 627 (1923).
(14) Powell, A. R., *J. Am. Chem. Soc.*, 45, 1 (1923).
(15) Ralston, O. C., Bur. Mines, *Tech. Paper* 93, 12 et seq. (1915).
(16) Ray, A. B., *Chem. & Met. Eng.*, 28, 977 (1923).
(17) Schrauth, W., *Brennstoff-Chem.*, 4, 161 (1923).
(18) Violette, *Ann. chim. phys.*, 32, 322 (1853).
(19) Warren and Storer, *Mem. Am. Acad.*, [2] 9, 208 (1865); Mabery and Hudson, *Am. Chem. J.*, 19, 482 (1897); *Proc. Am. Acad.*, 36, 266 (1901).
(20) Washburn, E. W., *Bur. Standards J. Research*, 2, 482 (1929).
(21) Willstätter, R., and Kalb, L., *Ber.*, 55, 2637 (1922).

RECEIVED September 7, 1933.

GASOLINE FROM COAL TO BE PRODUCED BY STATE-OWNED PLANT IN SAXONY. A plant to produce gasoline from coal will be constructed and operated by the State Government of Saxony if present plans materialize, according to a report from the Consul at Dresden, submitted to, and made public by the Commerce Department.

The manufacture of gasoline, the report shows, is to be based on the resources of the State-owned mine in Bohlen. The new enterprise is to be in line with a national motorization scheme developed by the present German régime. Its close coördination with the national scheme is supported by the fact that the central government has offered to furnish 5,000,000 reichsmarks, the initial capital required for plant construction.

It is proposed to convert approximately 600 tons of lignite into gasoline daily by a special process, it is stated. The annual output of gasoline from the plant is forecast at between 5000 and 20,000 metric tons. At present, Germany depends largely upon imported gasoline. It is anticipated that total consumption in 1933 will amount to 1,360,000 metric tons, of which 830,000 tons valued at 200 million reichsmarks will have to be imported. A marked increase in gasoline consumption is predicted for 1934 as a result of recent developments in highway construction, reduction of taxes, and other government measures. In the interest of national economy, therefore, Germany has a strong desire to produce its own motor fuel.

Compared with the total national demand for gasoline, production of 20,000 tons annually from soft coal does not appear important. As a beginning, however, it is important, since sufficient raw material exists in Germany for the production of the largest part of the country's gasoline requirements.

Physical Factors Governing Cracking Operations

George Granger Brown, University of Michigan, Ann Arbor, Mich., Warren K. Lewis, and
Harold C. Weber, Massachusetts Institute of Technology, Cambridge, Mass.

The information available on the P-V-T relations of hydrocarbons is reviewed, methods based on these relations for calculating important thermal properties of hydrocarbon and hydrocarbon mixtures are indicated, and computation methods for evaluating the conditions existing at equilibrium in vapor-liquid mixtures are pointed out. Special emphasis is laid on the extrapolation of these methods and their application to the solution of cracking plant problems.

ONE of the most important factors in the greatly increased efficiency achieved in cracking processes during the last fifteen years has been improvements in the methods of separation of vapor from liquid in the cracked products or in the feed. During the period, the pressures and temperatures in the separation operation have steadily increased and have now reached a point where the computation methods satisfactory under former conditions are no longer adequate for requirements of modern design. Further progress in process improvement will probably not be achieved by the empiricism of the past but must be based on a sound, quantitative analysis of the influence of operating conditions. Such an analysis is possible only in case one has an adequate knowledge of vapor-liquid equilibria and of heat effects.

Developments during the last two or three years make it possible to analyze these factors, complex though they be, with ever increasing certainty. It is the purpose of this article to review the information on physical properties of hydrocarbons which must serve as the necessary basis for this analysis and to indicate the methods by which it can be employed to aid in design or operation.

During recent years the work of a number of investigators has made it appear that the P-V-T relations of all hydrocarbons are strikingly similar when considered on a comparable basis. The basis of comparison is the critical condition of the individual pure hydrocarbon. Calling the critical pressure P_c, temperature T_c, and volume V_c for the hydrocarbon in question, its pressure, P, may be expressed in terms of the critical pressure as P/P_c. This ratio is called the "reduced pressure," P_r. Similarly the reduced temperature $T_r = T/T_c$, and the reduced volume $V_r = V/V_c$. Within the precision of present data the reduced volume of any hydrocarbon with more than three carbon atoms per molecule may be considered a unique function of reduced pressure and temperature—i. e., $V_r = f(P_r, T_r)$, where f represents the same function for all higher hydrocarbons. This relationship is equivalent to saying that such hydrocarbons obey a common, reduced equation of state. The equation can be written in a different and, for engineering purposes, more convenient form by the introduction of a correction factor, Z, or μ, in the gas laws, $PV = NZRT$. For an ideal gas $Z = 1$. A common reduced equation of state is equivalent to saying that Z is a unique function of P_r and T_r, for all higher hydrocarbons. Figure 1 shows this compressibility factor, Z, plotted against P_r for various values of T_r. If the critical temperature and pressure of the hydrocarbon in question are known, the value of Z may be obtained for any desired value of P and T from this plot. By inserting this value into the equation $PV = NZRT$, the P-V-T relation for any higher hydrocarbon may be obtained.

Unfortunately the data available on higher hydrocarbons under conditions where the deviations from the gas laws are great are extremely meager. The relationships in the case of three important hydrocarbons are shown in Figure 2. Along the low-temperature isotherms, the high-molecular-weight isopentane gives values of Z lower than the low-molecular-weight methane and ethylene, whereas along high-temperature isotherms the reverse is true. Along the critical these differences tend to disappear, and they apparently are relatively less for the hydrocarbons of higher molecular weight; thus, little if any appreciable error is introduced if all hydrocarbons of over three carbon atoms are treated by this common plot. As additional data needed on these higher hydrocarbons are obtained, it will perhaps be found that corrections should be applied for compounds of high molecular weight and boiling point, but at the present time data to make such corrections accurately are not available. Therefore, for all hydrocarbons having more than three carbon atoms per molecule, the use of Figure 1 is recommended.

To employ these methods requires a knowledge of the critical temperature and pressure of the individual hydrocarbon with which one is working. For the lower hydrocarbons these data are available (*1*, *2*, *3*), but for those of higher molecular weight experimental determination is out of the question because of thermal instability. Clearly, therefore, methods of estimation of the critical conditions of the individual hydrocarbons are necessary. Charts that appeared recently in a paper by Watson and Nelson (*5*) for estimating the critical temperature, combined with a reliable vapor pressure chart (*3*), provide the most convenient and reliable means of estimating critical temperatures and pressures.

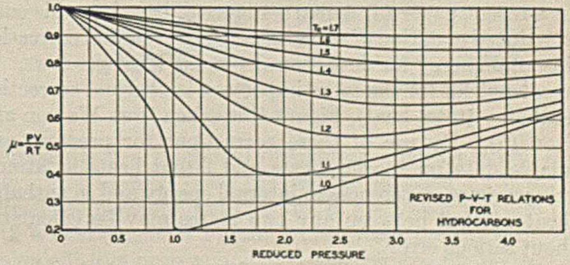


Figure 1

Knowledge of the P-V-T relations of any material makes possible the calculation of certain important relationships between the thermal properties, equilibrium between vapor and liquid, and conditions of temperature and pressure. In the case of any substance which does not deviate materially from the ideal gas laws, the relations are extraordinarily simple. In the first place, the internal energy is a function of the temperature only, independent of pressure and volume, and is equal to $\int C_v dT$ on the basis of unit mass or $\int MC_v dT$ per mole. Furthermore, the specific heat at constant pressure is also a function of temperature only, completely independent of pressure and volume. Change in enthalpy (total heat or heat content) is therefore equal to $\int C_p dT$ on the basis of unit mass or $\int MC_p dT$ per mole. These relationships have in the past been used almost universally in calculating the thermal

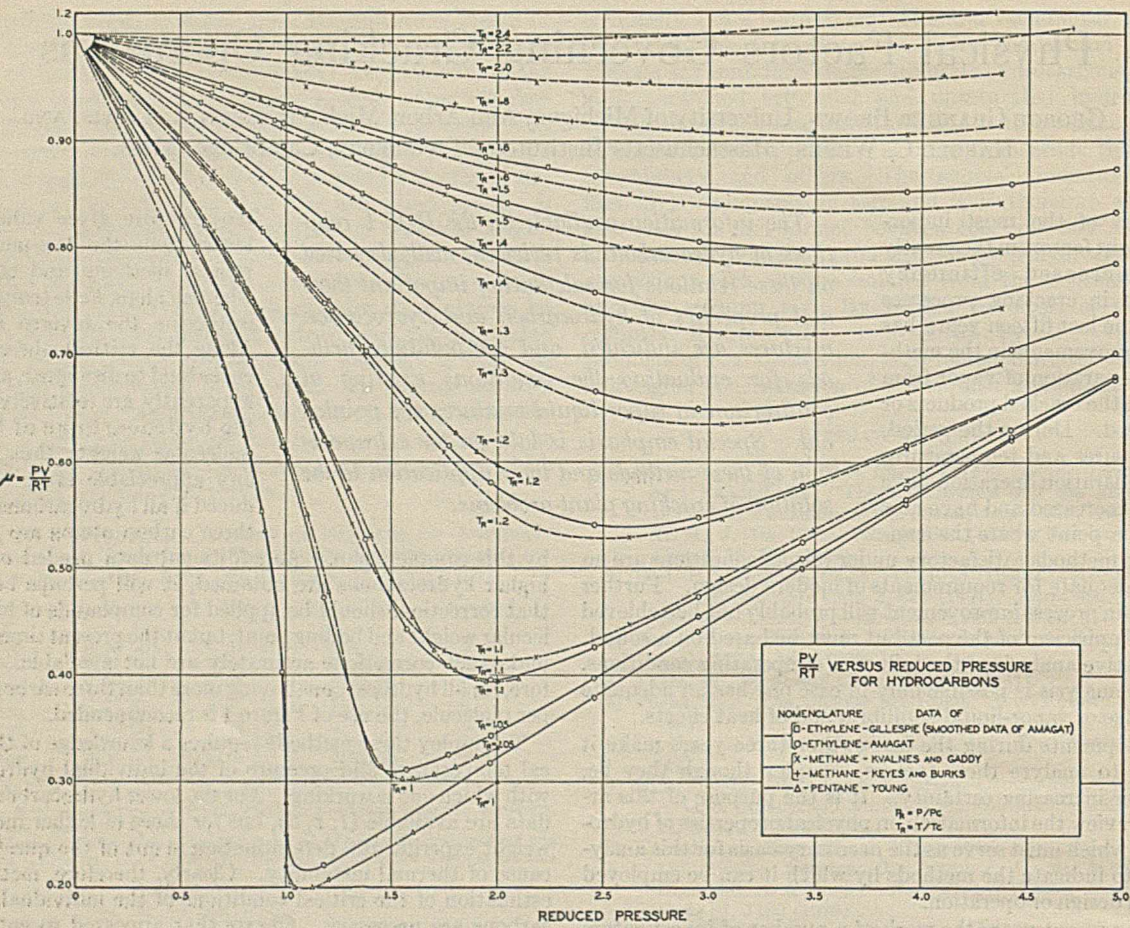


Figure 2

behavior of petroleum gases and vapors, but they introduce serious error as soon as one is dealing with pressures sufficiently high for the deviations from the gas laws to be serious.

In a recent paper (*4*) a chart, Figure 3, based on this common reduced equation of state, gives the isothermal correction to internal energy for deviations from the ideal gas laws. A convenient plot for the more important isothermal correction to enthalpy (total heat), Figure 4, is taken from Watson and Nelson (*5*). By use of these corrections for pressure and available data on specific heats and latent heats at atmospheric pressure, differences in internal energy and in enthalpy or heat content between any two states may be calculated without serious error.

In the past the petroleum engineer has calculated heat effects on the assumption that deviations from the ideal gas laws could be neglected for all vapors. He has available numerous formulas, charts, and tables for the specific heats of liquid hydrocarbons, for latent heats of vaporization, and for specific heats of hydrocarbon vapors (*5*), all of which are based on low-pressure measurements. These methods of calculation are relatively satisfactory if the whole operation is, in fact, conducted at low pressure. However, none of these data or methods makes allowance for the influence of pressure on the operation. The charts just mentioned serve to make exactly this correction and can be used in conjunction with the customary procedure. The heat effect of the change in question is calculated by the methods hitherto employed, from the initial to the final temperature, but at pressures low enough so that deviations from the gas laws can be neglected—e. g., atmospheric or below—and then the final result is corrected by the use of these charts. If the material is in the vapor state at but one end of the operation, the correction need be applied at this end only, as no correction for pressure on liquids is usually necessary.

In heating and evaporating a liquid followed by superheating the vapor, the heat quantity required may be computed as the sum of the sensible heat in liquid up to the boiling point under an applied pressure at which the latent heat and heat capacity of vapor are known, plus the known latent heat at this temperature and pressure, plus sensible heat in superheating the vapors to the final temperature, plus the isothermal increase in enthalpy of the vapor at the final temperature between the vaporizing pressure and final pressure, using data such as are given in Figure 4.

In this connection, increase in pressure at constant temperature and the corresponding decrease in volume of a vapor always result in a decrease in both internal energy and enthalpy. In other words, the corrections are always negative for an increase in pressure.

Relatively little difficulty is experienced in treating single pure hydrocarbons, but the petroleum engineer is interested primarily in mixtures usually of great complexity, particularly so in cracking operations.

Mixtures

Although the data on P-V-T properties of hydrocarbon mixtures are extremely meager and lacking almost entirely in the case of the higher hydrocarbons, the known facts point to the advisability of using the mixture rule of Amagat; namely, when a vapor is formed by mixing other vapors at constant temperature and pressure, the volumes are additive. This assumption is equivalent to that of assuming ideal solutions and may also be applied with fair success to liquid solutions. Under these conditions or assumptions there is no heat effect on mixing, and the enthalpy of a vapor, or liquid, mixture is equal to the sum of the enthalpies of its components. Therefore, to calculate the enthalpy of a vapor mixture, the enthalpies of each of its components should be calculated at the temperature and total pressure of the mixture itself. The sum of these individual enthalpies is the enthalpy of the mixture.

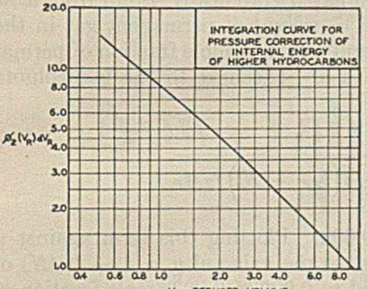


FIGURE 3

In dealing with mixtures, it should be remembered that hydrocarbon vapor formed from a solution of hydrocarbons is superheated in respect to the pure liquid hydrocarbon. For example, pentane vaporized from absorption oil at 10 pounds per square inch pressure is necessarily at a higher temperature than that required for pure pentane to develop a vapor pressure of 10 pounds per square inch. If the oil is heated from 100° to 300° F. at constant pressure in order to accomplish this vaporization of pentane, the heat required is equal to the total increase in enthalpy which may be computed over any of a number of paths with correct results, provided the initial and final states are correctly taken.

Thus, the heat required to raise the temperatures of the liquid oil is most easily determined as $\int_{100}^{300} WC_p dT$ where W represents the weight of oil. To this must be added the increase in enthalpy of pentane from liquid at 100° F. to vapor at 300° at 10 pounds per square inch pressure. This may be computed by a number of methods:

(1) Sensible heat liquid pentane 100° to 300° F. as $\int_{100}^{300} WC_p dT$ plus heat of vaporization from and at 300° F. and 10 pounds per square inch pressure.

(2) Sensible heat liquid pentane 100° F. to that temperature at which pentane exerts 10 pounds per square inch gage pressure (about 127°), plus latent heat of vaporization of pentane at 127° under its own vapor pressure of 10 pounds per square inch gage, plus sensible heat of pentane vapor under constant pressure of 10 pounds per square inch between 127° and 300° F.

(3) Sensible heat liquid pentane 100° to 300° F. $\left(\int_{100}^{300} WC_p dT\right)$, plus heat of vaporization at 300° and under pentane vapor pressure at 300° (about 220 pounds per square inch), plus the increase in enthalpy upon isothermal expansion at 300° from vapor pressure of pure pentane (about 220 pounds per square inch) to the total pressure at the final state (in this case 10 pounds per square inch gage) as given by a chart such as Figure 4.

The first method is the most convenient when the latent heats of the hydrocarbons under pressures other than the normal vapor pressure at any desired temperature are readily available. Unfortunately these data are usually lacking, but may be computed as suggested later. The second method depends upon the heat capacities of hydrocarbon vapors at pressures other than atmospheric. Although these data are not readily available, no difficulty is experienced at low pressures where the heat capacities at constant pressure may be taken as equal to the heat capacities at atmospheric pressure. The third method is convenient and satisfactory in all cases except when the final temperature is above the critical temperature of a component.

Similar calculations enable one to determine the heat of absorption of vapors in oils. By use of a chart such as Figure 4 in conjunction with available data on latent heat, vapor pressure, and heat capacity at atmospheric pressure, the differences in enthalpy between any two states of liquid and vapor may be computed.

This method is applicable even in the case of mixtures of great complexity. Such mixtures can be characterized by their true-boiling-point distillation curves, together with the molecular weight relationships. Thus, if for any weight fraction, w, the corresponding molecular weight is M and the corresponding enthalpy per mole, at the temperature and total pressure of the mixture, is H, the enthalpy of one pound of the mixture is equal to $\int \frac{Hdw}{M}$. This integral may be evaluated by plotting values of H/M as ordinates against the weight fractions and integrating, or measuring the total area under, the curve. This, or an equivalent method, may be employed for determining the enthalpies of high-pressure vapor mixtures such as those occurring in cracking operations.

Unless such methods are used which correct for deviations from the gas laws in any attempt to determine experimentally the heat of cracking at high pressure, the thermal data are likely to be misleading rather than helpful.

An apparent disadvantage to the use of this method is that it requires a fractional distillation analysis or true-boiling-point curve of the stock in question. With high-boiling stock this can be determined only by rectification under vacuum, but the effort is justified from other considerations, as a fractional distillation analysis is required for an adequate insight into the properties of mixtures. Fairly satisfactory results may be obtained by an empirical relationship between A. S. T. M. distillation and composition for a limited number of components if a fractional distillation analysis is not available. But in such cases the results obtained by using the critical temperature and pressure of the vapor mixture itself with a chart such as Figure 4 (assuming the mixture to be equivalent to a pure compound) as suggested by Watson and Nelson (*5*) are usually sufficiently accurate for present engineering requirements, because the correction to be added for a change in pressure is small as compared with the increase in enthalpy with temperature, and far more convenient.

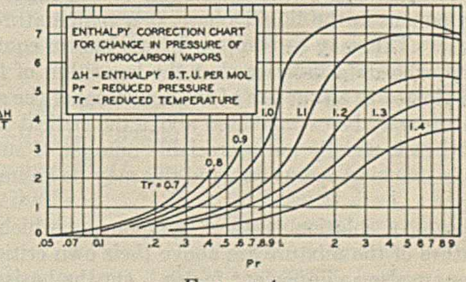


FIGURE 4

EQUILIBRIUM BETWEEN VAPOR AND LIQUID

When treating single compounds, the equilibrium between vapor and liquid is obtained from the vapor pressure relationships. But when dealing with mixtures, particularly at high pressure, other methods must be used if reliable results are to be obtained (*1*, *2*, *3*).

From the P-V-T relationship the fugacities of pure hydrocarbon vapors and correspondingly of the liquids in equilibrium with them may be obtained (*1*, *2*). If the ideal solution laws may be applied to mixtures of liquid hydrocarbons as well as to vapor mixtures, the equilibrium between liquid and vapor may be calculated by means of the fugacities (*1*, *2*).

The fugacity chart, Figure 5, based on the P-V-T data of Figure 1 may be used by writing $yf_v = xf_L$ or:

$$\frac{y}{x} = \frac{f_L}{f_v} \text{ for an equilibrium vaporization}$$

where y = mole fraction in vapor
x = mole fraction in liquid
f_v = fugacity of pure vapor at temperature and total pressure of equilibrium
f_L = fugacity of pure liquid at temperature and total pressure of equilibrium

Actually the fugacity of the pure liquid may be taken at the saturation pressure with greater convenience and without appreciable error.

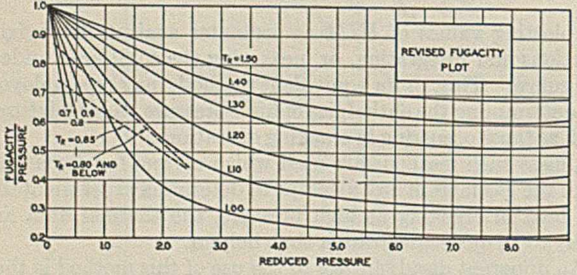


FIGURE 5

These relationships assume that the laws of ideal solutions apply to liquid as well as vapor mixtures of hydrocarbons. Actually there are deviations (*3*) which must be considered for precise calculations on individual compounds, but in complex mixtures such as occur in cracking operations, such refinements appear unnecessary.

A difficulty in applying the fugacities directly to an equilibrium computation is the estimation of the fugacity of a pure component in the liquid phase at a temperature above its critical. This may be computed from known equilibrium data, and such data indicate that the logarithm of fugacity of liquid plotted as a function of the reciprocal of the absolute temperature may be extrapolated above the critical temperature. There is usually an appreciable number of such components in cracking operations, and this may be an important difficulty.

The heats of solution of these components which at the temperature of the mixture are above their own critical temperatures are also an important factor. On the basis of ideal solutions and the extrapolated fugacity just discussed, the heat of solution is the decrease in enthalpy, corresponding to isothermal compression of the gas, from the temperature and total pressure at which it actually exists in contact with the liquid to that pressure corresponding to the fugacity of the component in the liquid state.

The following data represent the true-boiling-point curve of a stock with an extremely wide range and the tabulation shows the technic of calculating the performance of this stock for a specified set of conditions using the fugacity chart directly. Column 1, Table I, shows the weight per cent at the temperature of column 2 on the true-boiling-point curve; the molecular weight is given in column 3. The substantially permanent gas per pound of total mixture is about 0.00038 mole. The average molecular weight of the mixture is 176. The first line of figures in these columns is estimated by extrapolation. The calculations are made to determine the compositions and amounts of the vapor and of the nonvaporized liquid which will result from heating this stock to 900° F. under a pressure of 35 atmospheres (515 pounds per square inch absolute). The formula is as follows:

$$y = \int \frac{dw}{MN + \left(\frac{1}{M_0} - N\right) f\pi/f_P} = \frac{N - n}{N}$$

The formula is based on one pound of mixture, including gas, if any. The integral, evaluated graphically, is not from w = 0 to w = 1, but from w = weight of permanent gas in the total mixture to w = 1, and y = 1 − mole fraction of permanent gas in the vapor phase. The next to the last column of figures is the term,

$$\frac{1}{MN + \left(\frac{1}{M_0} - N\right) f\pi/f_P}$$

for the value of N = 0.003. Plotting this term against w and obtaining the area gives the value of $y = 1 - (n/N)$ of 0.873, which, when added to 0.00038/0.003 (mole fraction of gas), gives unity. In other words, in this case the mole fraction of the original stock evaporating is 0.003/0.00568 = 53 per cent.

It is instructive to compare the values of π/P with those of $f\pi/f_P$ for this case. At the upper end of the boiling range the ratio of the two is over 4:1. In the middle of the range, it is lower, and at the lower end of the data the ratio becomes less than one. The character of the errors introduced by ignoring the deviations from the gas laws is obvious.

Another method of treatment (*1*) is to plot the ratio $y/x = K$ as a logarithmic function of temperature at different pressures for each compound (*3*) and read the value for y/x directly for any temperature and pressure. Such plots lend themselves readily to extrapolation above the critical and have been drawn to include high temperatures, and to allow for the effect of pressure on fugacity of liquid and for individual deviations from the general plot, Figure 1. These charts avoid the necessity of estimating critical temperatures and pressures as must be done in using the fugacity chart (Figure 1) directly.

The heat of solution of a vapor or gas into a liquid may be readily estimated for any temperature or pressure condition, above or below the critical, by taking the slope of log K plotted as a function of temperature and using the well-known van't Hoff equation:

$$\frac{d \log_e K}{dT} = \frac{\Delta H}{RT^2}$$

The use of the equilibrium constants has been described in a recent article (*3*). When applied to the same stock and conditions as given in Table I, the computation indicated that 51.3 per cent by weight was vaporized, compared with 53 per cent by use of the fugacity chart directly on only four liquid components. These results compare with an experimental value taken at another time, but under similar conditions, of 55 per cent by volume or about 51.5 per cent by weight.

TABLE I. CALCULATION OF THE PERFORMANCE OF A STOCK FROM A FUGACITY CHART

W	T °F.	M	$1/M$	T °C.	P*	P_c	P_r	π_r	T_c °C.	T_c (°K.)	T_r	$\frac{f_P}{P}$	$\frac{f\pi}{\pi}$	f_P	$f\pi$	$\frac{f\pi}{f_P}$	$\frac{1}{MN + \left(\frac{1}{M_0} - N\right)\frac{f\pi}{f_P}}$	π/P
100	1200	515	0.00194	649	30	13,500	0.0022	1.97	800	(1073)	0.703	1.00	0.21	30	5,580	186	0.0039	886
70	685	239	0.00418	363	7,000	16,800	0.417	1.58	560	(833)	0.906	0.78	0.41	5,450	10,900	2.00	0.50	3.8
40	557	193	0.00517	292	20,000	20,000	1.00	1.33	482	(755)	1.00	0.65	0.53	13,000	14,100	1.09	0.88	1.33
10	360	135	0.00741	182	42,900	245,000†	1.75	1.08	385	(658)	1.15	0.65	0.77	27,900	20,500	0.74	1.50	0.62

* At 900° F. = 482° C. = 755° K. † Estimated.

Nomenclature

w = weight fraction in total mixture boiling up to a given temp., t, and hence is the pounds in the total mixture whose true boiling points lie below this temperature
N = vapor (including permanent gas, if any) in the mixture under the conditions in question, moles
M_0 = av. mol. weight of the total mixture
M = mol. weight of a given narrow fraction, dw, of boiling point t
n = inert (essentially insoluble gas) in the mixture, moles
P = vapor pressure of the component in question at temp. of the mixture
π = total pressure on the mixture
f = fugacity of a given component at temp. of the mixture
f_P = fugacity at temp. of the mixture under saturation pressure, P, of a given component
f_π = fugacity at temp. of the mixture under total pressure, π, of a given component

Literature Cited

(1) Brown, Souders, Smith, and Selheimer, Ind. Eng. Chem., 24, 513 (1932).
(2) Cope, Lewis, and Weber, *Ibid.*, 23, 887 (1931).
(3) Katz and Brown, *Ibid.*, 25, 1373 (1933).
(4) Lewis and Luke, *Ibid.*, 25, 725 (1933).
(5) Watson and Nelson, *Ibid.*, 25, 880 (1933).

Received September 7, 1933.

(This Symposium Was Begun in the January Issue and Concluded in This Issue.)

New Table of the Refractive Index of Pure Glycerol at 20° C.

L. F. Hoyt, Larkin Company, Inc., Buffalo, N. Y.

The refractive index of glycerol of unusual purity has been determined at thirty-one different concentrations by means of the multiple-prism dipping refractometer. From these observed values a new table of the refractive index of pure glycerol of 20.0° C. is constructed, showing the refractive index of glycerol for each per cent from 1 to 100. With the aid of this table and by using a bath controlled within ±0.1° of 20.0° C. it is possible to determine easily and quickly the concentration of pure aqueous solutions of glycerols within 0.1 per cent.

The refractive index of 100 per cent pure glycerol at 20.0° C. has been found to be 1.47399; its coefficient of refractive index per 1° C. over the range from 10° to 20° C. is 0.000225.

THERE are recorded in the literature four tables showing the refractive index of glycerol at various concentrations. Lenz (*5*) published in 1880 the first table which gives the refractive index of glycerol over the complete range from 1 to 100 per cent at 12.5° to 12.8° C. Lenz constructed his table from observations on only ten samples of diluted glycerol which he prepared from a pure glycerol of 96.04 per cent strength whose concentration he checked by elementary analysis. Lenz estimated that the concentration of glycerol could be determined with the aid of his table with an accuracy of about 0.5 per cent from an observation of its refractive index in the Abbé refractometer. In 1884 Strohmer (*8*) published a similar table, covering however only the range from 50 to 100 per cent at 17.5° C. Strohmer prepared about thirty dilutions from a quantity of crystallized glycerol whose composition by elementary analysis coincided very closely with the formula of 100 per cent $C_3H_8O_3$. In 1885 Skalweit (*7*) introduced another table of the refractive index of glycerol at 15° C., covering the entire range from 1 to 100 per cent. Skalweit gives few details concerning the diluted glycerols whose refractive index he determined, except to state that he had available numerous samples, prepared from a large quantity of crystallized glycerol, whose specific gravities and hence concentration he had accurately determined. In 1925 Iyer and Usher (*4*) published a table showing the refractive index of glycerol at 25° C. This table however gives only the refractive index values at intervals of concentration of 5 per cent. In preparing their diluted samples, Iyer and Usher used Merck's c. p. glycerol whose concentration they determined by specific gravity to be 97.75 per cent, but they do not state the reference table used in determining this critical value. They prepared what they considered to be a 100 per cent glycerol by blowing dry air through their 97.75 per cent glycerol maintained at 90° C. until its refractive index became constant.

All four of these tables were prepared with the aid of the Abbé refractometer which reads to 0.0001 but is of somewhat doubtful accuracy in the fourth decimal place. Thus while convenient, rapid, and applicable to only a few drops of material, the refractive index of glycerol as determined by the Abbé refractometer is distinctly less accurate as a method of determining the concentration of glycerol than is the specific gravity method.

The immersion or dipping refractometer was developed just prior to 1900 by the firm of Zeiss at Jena. As originally introduced, this was a single-prism instrument covering the limited range from 1.32776 to 1.36674, having an arbitrary scale reading from −5° to 105°, and provided with a vernier reading to 0.1°. With this instrument it is easily possible to observe differences in refractive index of the order of 0.00004. By 1907 a considerable literature had developed on the uses of this valuable instrument, and the available data were published in a book (*9*) containing about eighty tables for the quantitative estimation of organic and inorganic substances; Table 70 gives the refractive index of dilute glycerol solutions at 17.5° C. over the range from 0 to 28.72 grams per 100 cc. This table is a refinement and extension by Wagner of a similar table published in 1905 by Henkel and Roth (*2*).

Since 1927 an improved dipping refractometer with six interchangeable prisms has been available. The instrument provides an extremely accurate and sensitive method of determining refractive index over the extensive range from 1.32539 to 1.54581.

Early in 1933 Hoyt (*3*) published some data showing the refractive index at 20.0° C. as determined by the multiple-prism dipping refractometer of a series of twelve samples of diluted glycerols ranging in concentration from 25 to 99.8 per cent, the samples being prepared by dilution of a glycerol of exceptional purity.

This work has been continued and elaborated to include additional dilutions at intervals over the entire range from 0 to 100 per cent glycerol, and from the data so obtained a new table has been constructed showing the refractive index of glycerol at 20.0° C. to 0.00001 from 0 to 100 per cent, using the dipping refractometer.

Determination of Refractive Index

The earlier work of Hoyt with the dipping refractometer was carried out at a time when laboratory temperatures remained remarkably constant at 20° C. because of favorable weather conditions.

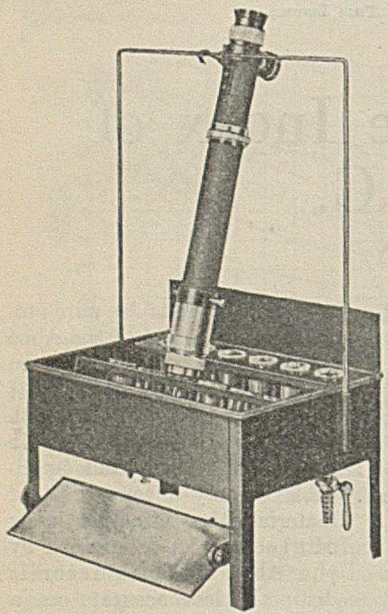


Figure 1. Bausch and Lomb Dripping Refractometer with Heating Trough

The dipping refractometer is so sensitive that, in order to secure reliable and reproducible results, the temperature at which observations are made must be controlled within ±0.1° C. of the chosen temperature.

Through the courtesy of the Bausch and Lomb Optical Company there was placed at the author's disposal for this work a multiple-prism dipping refractometer and a new type of temperature control device of their own design, only recently available. Observations with the dipping refractometer are made in small glass beakers, or in a special metal beaker fastened to the instrument, in a water bath shown with the instrument in Figure 1. The new Bausch and Lomb temperature control device shown in Figure 2 provides a means of maintaining a flow of water at a practically constant temperature through the bath. This device consists essentially of an enameled steel cylindrical chamber mounted inside a slide wire rheostat. Water from the tap is supplied at constant head through a 27-inch (68.6-cm.) standpipe. In addition to the heating adjustment provided by the slide wire rheostat, there is a microadjustment on the valve between the standpipe and the heating chamber. In this way a very sensitive adjustment is readily obtained. This heat control device was found to function admirably. With the heating element operating continuously at minimum, with tap water at 15° C., and with a flow of about 1200 cc. per minute through the bath which the apparatus delivers with the microvalve wide open, it was found that a temperature of 20.0° C. constant to within ±0.1° C. could be maintained for hours with only occasional minor adjustments quite independent of the fact that the air temperature in the room where the work was being conducted ranged from 28° to 32° C. In cases where it might be found impracticable to secure a flow of 1200 cc. or more of water through a bath owing to the restricted size of inlet and outlet orifices, this temperature control device may still be arranged to maintain the bath at not over 5° C. above that of the tap water supply (1) by increasing the head of water either by elevating the entire heat control device or lowering the overflow discharge of the bath, or (2) by the expedient of by-passing an additional amount of water through the heating device as follows: Interpose between the temperature control device and the bath a suction flask of any convenient size. The inlet of the water supply should be through a tube extending nearly to the bottom of the flask. Attach to the side arm of the suction flask a T tube, one arm of which is connected to the bath and the other to waste by a flexible rubber hose provided with a screw pinchcock. By using tubing of sufficient inside diameter, it is possible to by-pass enough water through the heating device to bring the total flow to 1200 cc. or more per minute and thus to reduce the temperature of the portion of the water flowing through the bath without interfering with the operation of the rheostat, already at minimum heat.

A supply of glycerol of unusual purity and high concentration was prepared in the Research Laboratory of the Procter and Gamble Company by fractional distillation of a double-distilled c. p. glycerol through a 48-inch (121.9-cm.) Vigreux column under 5 to 7 mm. pressure. The sample used represents the middle portion only of the distillate which exhibited a very constant boiling point. This glycerol had a specific gravity of 1.2616 (25°/25° C.) corresponding to a purity of 99.84 per cent, calculated from the table of Bosart and Snoddy (*1*).

From this glycerol were prepared thirty diluted samples ranging in concentration from 5 to 98 per cent. The proper amounts of glycerol and redistilled water were weighed into vials on an analytical balance, tightly stoppered, and sealed, and the samples were thoroughly mixed before any observations were made.

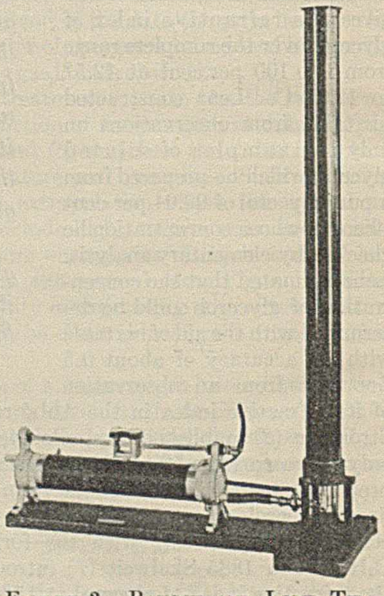


Figure 2. Bausch and Lomb Temperature Control Apparatus

The water bath used with the instrument was maintained for all tests within ±0.10° of 20.0° C., and observations were taken only when the bath ranged between 19.95° and 20.05° C. Under such conditions, after the sample had assumed the temperature of the bath, it was found that successive readings with the instrument consistently checked within 0.1° C. of the scale. To avoid any possible change of concentration of the glycerol samples while under observation, as could easily occur if the more concentrated samples of this hygroscopic material were examined in the open beakers ordinarily used, the metal beaker which screws tightly on to the instrument was used in every case.

Successive readings were taken in groups of ten with the temperature maintained between 19.95° and 20.05° C. at intervals of about 10 minutes until the averages of such readings checked within 0.1° C. on the instrument scale. Since 0.1° is the limit to which the instrument can be read, it is probably of doubtful accuracy to report averages of results beyond that figure.

Each time prisms are interchanged on the instrument, it is necessary of course to adjust the instrument to a correct reading with the test solutions or test pieces provided for each prism. Table I gives the observed values for the various dilutions.

TABLE I. REFRACTIVE INDICES OF DILUTED GLYCEROL SAMPLES

GLYCEROL	PRISM USED	REFRACTOMETER READING (20.0° C.)	REFRACTIVE INDEX
% by weight			
Water	A	14.4	1.33303
4.95	A	29.5	1.33888
6.47	A	33.5	1.34041
9.87	A	44.5	1.34459
10.46	A	46.6	1.34539
14.69	A	60.5	1.35060
19.73	A	77.9	1.35700
20.77	A	81.5	1.35832
25.04	A	97.6	1.36412
29.86	B	9.9	1.37021
29.89	B	10.5	1.37045
34.39	B	25.3	1.37626
39.60	B	44.3	1.38360
44.40	B	60.7	1.38981
49.75	B	81.1	1.39741
49.91	B	82.6	1.39796
54.42	C	10.0	1.40428
57.80	C	24.8	1.40981
59.54	C	31.5	1.41230
64.38	C	49.4	1.41882
69.31	C	72.4	1.42702
69.84	C	73.7	1.42748
74.41	C	92.4	1.43400
79.73	D	10.9	1.44217
85.13	D	35.5	1.45124
89.87	D	53.4	1.45760
92.10	D	64.4	1.46161
94.98	D	76.3	1.46579
95.26	D	78.0	1.46638
97.38	D	86.5	1.46932
98.80	D	93.1	1.47159
99.84	D	99.2	1.47367

TABLE II. REFRACTIVE INDEX OF GLYCEROL AT 20.0° C.

GLYCEROL	REFRACTIVE INDEX	DIFFERENCE FOR 1%	GLYCEROL	REFRACTIVE INDEX	DIFFERENCE FOR 1%
% by weight	n_D^{20}		*% by weight*	n_D^{20}	
100	1.47399	0.00165	50	1.39809	0.00149
99	1.47234	0.00163	49	1.39660	0.00147
98	1.47071	0.00161	48	1.39513	0.00145
97	1.46909	0.00157	47	1.39368	0.00141
96	1.46752	0.00156	46	1.39227	0.00138
95	1.46597	0.00154	45	1.39089	0.00136
94	1.46443	0.00153	44	1.38953	0.00135
93	1.46290	0.00151	43	1.38818	0.00135
92	1.46139	0.00150	42	1.38683	0.00135
91	1.45989	0.00150	41	1.38548	0.00135
90	1.45839	0.00150	40	1.38413	0.00135
89	1.45689	0.00150	39	1.38278	0.00135
88	1.45539	0.00150	38	1.38143	0.00135
87	1.45389	0.00152	37	1.38008	0.00134
86	1.45237	0.00152	36	1.37874	0.00134
85	1.45085	0.00155	35	1.37740	0.00134
84	1.44930	0.00156	34	1.37606	0.00134
83	1.44770	0.00160	33	1.37472	0.00134
82	1.44612	0.00162	32	1.37338	0.00134
81	1.44450	0.00160	31	1.37204	0.00134
80	1.44290	0.00155	30	1.37070	0.00134
79	1.44135	0.00153	29	1.36936	0.00134
78	1.43982	0.00150	28	1.36802	0.00133
77	1.43832	0.00149	27	1.36669	0.00133
76	1.43683	0.00149	26	1.36536	0.00132
75	1.43534	0.00149	25	1.36404	0.00132
74	1.43385	0.00149	24	1.36272	0.00131
73	1.43236	0.00149	23	1.36141	0.00131
72	1.43087	0.00149	22	1.36010	0.00131
71	1.42938	0.00149	21	1.35879	0.00130
70	1.42789	0.00149	20	1.35749	0.00130
69	1.42640	0.00149	19	1.35619	0.00129
68	1.42491	0.00149	18	1.35490	0.00129
67	1.42342	0.00149	17	1.35361	0.00128
66	1.42193	0.00149	16	1.35233	0.00127
65	1.42044	0.00149	15	1.35106	0.00126
64	1.41895	0.00149	14	1.34980	0.00126
63	1.41746	0.00149	13	1.34834	0.00125
62	1.41597	0.00149	12	1.34729	0.00125
61	1.41448	0.00149	11	1.34604	0.00123
60	1.41299	0.00149	10	1.34481	0.00122
59	1.41150	0.00149	9	1.34359	0.00121
58	1.41001	0.00149	8	1.34238	0.00120
57	1.40852	0.00149	7	1.34118	0.00119
56	1.40703	0.00149	6	1.33999	0.00119
55	1.40554	0.00149	5	1.33880	0.00118
54	1.40405	0.00149	4	1.33762	0.00117
53	1.40256	0.00149	3	1.33645	0.00115
52	1.40107	0.00149	2	1.33530	0.00114
51	1.39958	0.00149	1	1.33416	0.00113
			0	1.33303	.....

When the observed values of Table I were plotted on a sufficiently large scale, they were found to fall along a curve which deviated somewhat from the straight line drawn between the refractive indices of pure water and pure 100 per cent glycerol. Examination of this curve showed that it could be divided into three sections—viz., a curve from 0 to 44 per cent concentration, inclusive, and another curve from 80 to 100 per cent concentration, both of which are represented by third-degree equations, while the central portion from 45 to 79 per cent, inclusive, was found to be practically a straight line. The equations for these various portions of the refractive index–concentration curve were found to be as follows:

I. Curve from 0 to 44 per cent glycerol, inclusive,
$y = 1.33303 + 0.001124x + 0.00000605x^2 - 0.0000000555x^3$
II. Straight line from 45 to 79 per cent glycerol, inclusive,
$y = 0.00149x + 1.32359$
III. Curve from 80 to 100 per cent glycerol, inclusive,
$y = 0.90799 + 0.0154x - 0.000155x^2 + 0.000000576x^3$

From these three equations the values of the refractive index of glycerol for each per cent from 1 to 100 were computed and are shown with the differences in refractive index for each per cent glycerol in Table II.

The values of refractive index for each concentration of glycerol in Table I were calculated from the proper equation and were found to deviate from the observed values on the average by only 0.00011. Since a change in concentration of glycerol of 1 per cent is equivalent on the average to a change of refractive index of 0.00141, the calculated values shown in Table II should permit the determination of the concentration of glycerol within at least 0.1 per cent.

The effect of temperature on the refractive index of pure glycerol of high concentration (99.84 per cent) was studied by taking observations of refractive index over a range of temperature from 10° to 20° C. The observed values are shown in Table III.

TABLE III. REFRACTIVE INDEX OF PURE GLYCEROL (99.84 PER CENT) AT VARIOUS TEMPERATURES

(All readings made with prism D)

TEMP.	SCALE READING	n/D	TEMP.	SCALE READING	n/D
° C.			*° C.*		
10.2	105.9	1.47592	15.0	102.7	1.47485
11.2	105.4	1.47575	15.8	102.1	1.47464
12.2	104.7	1.47552	17.6	100.7	1.47418
12.8	104.2	1.47536	18.0	100.4	1.47408
13.8	103.5	1.47512	20.0	99.2	1.47367

Table III shows that the coefficient of the refractive index of pure glycerol (99.84 per cent) averages 0.000225 per 1° C. over a range from 10° to 20° C. This value is lower than has previously been reported in the literature for high-concentration glycerol. Wolff (*11*) found a change in the refractive index of very pure glycerol of 86 per cent concentration of 0.00028 over the temperature range 12.5° to 17.5° C., while van der Willigen (*10*) in 1869 reported coefficients of refractive index of glycerol per 1° C. ranging from 0.00021 for glycerol of about 44 per cent concentration to 0.00025 for glycerol of about 90 per cent concentration. Listing (*6*) in that same year reported a change of refractive index per 1° C. of 0.00032 for glycerol of about 96 per cent concentration. Obviously the coefficient of refractive index of glycerol is a function of concentration and would become numerically smaller with decreasing concentration, since the average coefficient of refractive index of pure water per 1° C. is 0.000081 over the range 10° to 20° C.

A difference in concentration of 1 per cent glycerol corresponds to a change of refractive index equivalent on the average to 0.00141 or practically 4° on the dipping refractometer scale. The change of refractive index of pure glycerol of high concentration with temperature is appreciable and amounts to 0.6–0.7° on the scale for each 1° C. The need for accurate control of temperature while making observations of the refractive index of glycerol with the dipping refractometer is obvious.

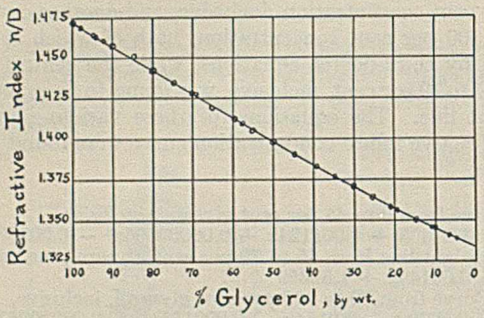


FIGURE 3. RELATION BETWEEN REFRACTIVE INDEX AND GLYCEROL CONCENTRATION

In some of the earlier work it was noticed that a long time interval—i. e., an hour or more—was often required to obtain constant readings of the high-concentration glycerols. This was probably due to the fact that in handling the instrument and its attached metal beaker the temperature of the sample under observation was raised above that of the bath. On account of favorable room temperature conditions which then prevailed, it was found possible to hold the bath temperature constant within less than 0.05° C. without a flow in water through the bath, but the sample under observation may have required a considerable time to assume the temperature of the motionless bath.

In the subsequent work with a bath maintained within 0.1° of 20.0° C. by means of the constant-temperature device it was found that the rapid flow of water (1000 cc. or more per minute) through the bath permitted constant readings to be obtained quickly and easily, even on the high-concentration samples.

ACKNOWLEDGMENT

The supply of glycerol of high purity and concentration used in these experiments was kindly supplied by J. T. R. Andrews of Procter and Gamble Company, chairman of the Glycerine Analysis Committee of the American Oil Chemists' Society. The author acknowledges his indebtedness to A. B. Osborne of the Engineering Department, Larkin Company, Inc., for his painstaking work in determining the equations and values of Table II.

LITERATURE CITED

(1) Bosart, L. W., and Snoddy, A. O., IND. ENG. CHEM., 19, 506 (1927).
(2) Henkel, H., and Roth, A. W., *Z. angew. Chem.*, 18, 1936 (1905).
(3) Hoyt, L. F., *Oil and Soap*, 10, No. 3, 43–7 (1933).
(4) Iyer, M., and Usher, F. L., *J. Chem. Soc.*, 127, 841 (1925).
(5) Lenz, W., *Z. anal. Chem.*, 19, 297–305 (1880).
(6) Listing, *Fortsch. Physik*, 1869, 294.
(7) Skalweit, J., *Repertorium anal. Chem.*, 5, 17 (1885).
(8) Strohmer, *Monatsh.*, 5, 55–62 (1884).
(9) Wagner, Tabellen zum Eintauchsrefraktometer, Sondershausen, 1907.
(10) Willigen, van der, *Fortschr. Physik*, 1869, 288; Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 6th ed., Vol. III, p. 403, Macmillan, 1923.
(11) Wolff, *Z. angew Chem.*, 32 I, 148 (1919).

RECEIVED August 16, 1933. Presented before the Division of Industrial and Engineering Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.

Der Alchymist im Laboratorium

by

THOMAS WYCK

(1617–1677)

No. 39 in the Berolzheimer Series of Alchemical and Historical Reproductions is from a painting in the Art Gallery in Dresden, Germany, and is the third in the series by Wyck, the others being Nos. 5 and 35. Wyck, who executed almost as many alchemical paintings as did David Teniers, the Younger, has a somber style which is all his own and resembles that of Adrian van Ostade much more than it does that of Teniers.

A complete list of the first thirty-six reproductions in the series, together with the details for obtaining photographic copies of the originals, will be found with No. 37 in our issue of January, 1934, page 112. No. 38 was reproduced in our February, 1934 issue, page 207. The photographs of these paintings are supplied in black and white only.

Rate of Drying Chrome Leather

O. A. Hougen, University of Wisconsin, Madison, Wis.

The general equation for the rate of drying chrome leather has been found experimentally to be:

$$\frac{dW}{d\Theta} = -\frac{0.282}{L} G^{0.6} W\Delta H$$

This equation holds for values of W below 1.25 and for values of G above 10. For values of W above 1.25 the rate of drying is constant. The average density of leather, excluding water, before drying is 0.46 and after drying is 0.50.

The methods of experimentally determining the drying coefficients of leather and deriving the above equation are described. The method of applying this equation to the progressive drying of leather is illustrated in problems for calculating drying time, length of drier, optimum air velocity, and the most economical fraction of recirculated air.

IN THE process of chrome leather manufacture the skin is dried after the sequence of tanning, fat-liquoring, and dyeing, and before the finishing operations of staking, tacking, graining, seasoning, and glazing. This intermediate drying operation is the one particularly referred to in this discussion. The purpose of this drying operation is to bring the tanned leather to a uniform state of dryness and to arrest all further chemical changes before completing the finishing operations of improving the appearance and handle of the product. After dyeing, the leather is hand-set. This operation consists of scraping off all loose surface water and at the same time stretching the leather in all directions to remove wrinkles and creases and to increase area. Following drying, the leather is piled in stacks and allowed to remain "in crust" for at least 12 hours. In this step the leather is cooled and regains moisture to reach equilibrium with the atmosphere. The leather is then dipped in water for 10 minutes to produce a slight but not thorough wetting. The wetted leather is sammied overnight by piling and covering with wet burlap. This period effects a uniform redistribution of water through the stock. After sammying, the skins are staked by machine to stretch them in all directions. The leather is then tacked on boards and dried before seasoning. The stock is dried again after seasoning previous to glazing and graining. This investigation deals solely with the drying operation after dyeing and hand-setting and not with the drying operation following tacking and after seasoning, although the same theory applies to all three drying operations, and the same drying coefficients are perhaps applicable.

The usual method of drying chrome leather is by means of a loft drier where the wet stock is suspended in a large room and allowed to remain until the desired dryness is obtained, drying being hastened by circulation of heated air. The modern trend in drying is toward the use of progressive driers wherein the wet stock is passed continuously through an enclosed tunnel countercurrent to a stream of heated air. The progressive drier has the advantages over a loft drier of being continuous in operation, requiring less handling, less labor, less space, less heat, and less time for drying, and of providing more nearly uniform drying conditions. The loft drier has the advantages of requiring less expensive equipment and of being more flexible in output and in time allotted. The original purpose of this investigation was to establish data for the design of a progressive drier in order to replace the less economical and slower method of loft drying.

Theory of Drying Applied to Leather

The drying of a fibrous material such as leather proceeds in three stages. When dried under constant drying conditions, the rate of drying remains constant during the first stage. In the second stage the rate of drying falls off directly with decrease in the free moisture content of the stock. In the third stage the rate of drying falls off more rapidly than the corresponding decrease in moisture content. By uniform drying conditions is meant that at any location on the surface of the leather the temperature of the stock and the temperature, humidity, velocity, and direction of the air stream remain constant. During the first stage of drying the entire surface of the stock is completely wetted; and, if evaporation proceeds adiabatically, the surface attains the wet bulb temperature of the air. In the second stage, evaporation is still restricted to the surface of the stock, but the actual wetted area decreases as drying proceeds, thereby resulting in a decreased rate of drying. During this stage diffusion of water is so rapid as to maintain a nearly uniform moisture concentration, and the water at the surface assumes a submicroscopic network exposing an effective wetted area proportional to the free moisture content of the stock. In the third stage of drying the surface of evaporation extends into the interior in which case there is no free moisture at the surface of the stock and vaporization proceeds over an increasing zone of thickness.

In the particular problem of drying leather involved in this investigation, only the second stage of drying need be considered. The period of constant drying rate is avoided by the operation of hand-setting whereby all free surface water is scraped off. Wherever permissible this mechanical removal of excess water is good practice. The mechanical removal of water by hydroextracting, wringing, or scraping requires much less energy than by application of heat for evaporation. The thickness of chrome leather is relatively small compared to the area exposed per pound of dry stock so that the resistance to diffusion of water is negligible compared to the resistance to diffusion of vapor into the surrounding air. The free moisture concentration of the stock remains nearly uniform. Experimentally it was found that under constant drying conditions the rate of drying decreased directly with the decrease in the average free moisture content of the stock and inversely with the thickness of the stock, so that for all practical purposes the problem of drying chrome leather may be treated as one involving only the second stage of drying. All experimental data obtained can be satisfactorily interpreted on this basis so that even though an appreciable concentration gradient exists through the stock, and the surface of evaporation extends into the stock, no justification is warranted in complicating the problem by consideration of these minor effects. Since the primary purpose of this investigation was to obtain data for the design and operation of progressive driers, it is undesirable and entirely unnecessary to increase unduly the complexity of mathematical treatment.

For this special case of drying, the fundamental drying equation reduces to the simple form derived by Walker, Lewis, and McAdams (*6*):

$$\frac{dW}{d\Theta} = -BW\Delta H \qquad (1)$$

where $B = \frac{mG^n}{L}$ (2)

W = free moisture content of stock
ΔH = unsaturation of air
G = mass velocity of air flowing over sheets
L = thickness of stock
Θ = time elapsed
m, n = experimental constants

Sherwood (*4*) and later McCready and McCabe (*2*) have shown that, when water diffusion is the controlling factor, evaporation is not restricted to the surface of the sheet, but that the surface of evaporation extends inward as drying proceeds, and that the mechanism of drying then involves three resistances—the diffusion of water through the stock up to the evaporation zone, the diffusion of vapor through the evaporation zone, and the diffusion of vapor through the air film adjoining the surface of the solid.

Furthermore, in the zone of vapor diffusion through the stock, evaporation proceeds through the entire thickness of this zone so that the flow of vapor increases as the outer surface is reached. The case of drying where liquid diffusion is the controlling factor and where vaporization occurs only at the surface of the sheet has been fully treated by Sherwood (*5*) and Newman (*3*).

EQUILIBRIUM MOISTURE CONTENT

When a hygroscopic material such as leather is suspended in unsaturated air, the water content of the leather changes until it comes into equilibrium with the air. This equilibrium moisture content increases with the relative humidity of the air, decreases slightly with increase in temperature, and is also dependent upon whether the material is losing or gaining moisture. For drying problems it is important to know the equilibrium moisture content when the stock is losing moisture, also called the "desorption moisture content." In plotting equilibrium moisture content, it is preferable to plot values against relative humidity rather than against percentage humidity since the former are independent of atmospheric pressure.

Values of the desorption moisture content of chrome leather are plotted in Figure 1 for both experimental and extrapolated values. In every case moisture content is expressed as a fraction of the weight of dry leather.

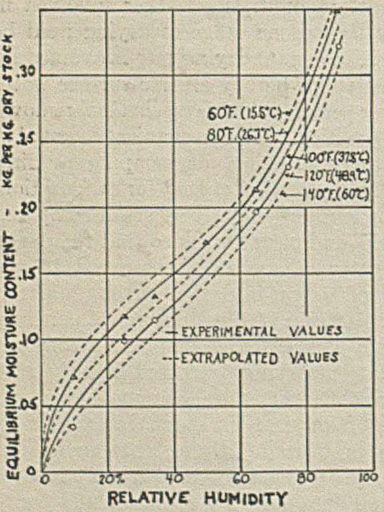


FIGURE 1. EQUILIBRIUM MOISTURE CONTENT OF CHROME LEATHER (DESORPTION VALUES)

The free moisture content can now be obtained from the relation:

$$W = T - E \qquad (3)$$

where T = total moisture content

EXPERIMENTAL PROCEDURE

It was the purpose of the experiments to establish values of the drying coefficient, B, to establish quantitatively the effect of air velocity, thickness of stock, and temperature of air upon this coefficient, and to determine the value of the constants, m and n, in Equation 2. An experimental drier was constructed large enough to dry thirty calfskins or kips.

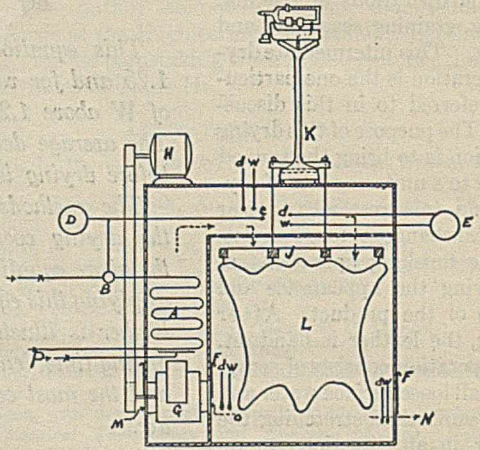


FIGURE 2. DIAGRAM OF EXPERIMENTAL DRIER

d. Dry-bulb thermometer
A. Heating coil
B. Steam inlet automatic control valve
C. Automatic temperature control thermometer
D. Temperature recorder
E. Humidity recorder
F. Shutter
G. Blower
w. Wet-bulb thermometer
H. Motor
J. Frame for supporting leather
K. Platform scale
L. Leather
M. Inlet for fresh air
N. Outlet for spent air
O. Opening for recirculated air
P. Live steam supply

This drier was of a compartment type, but, by recirculating a portion of the air, drying conditions could be made to simulate those in a progressive drier wherein the leather is progressively subjected to less humid air as drying proceeds. In this way, practical drying conditions are simulated, in contrast to the frequently used method of employing constant drying conditions in laboratory experiments. Using progressively changing drying conditions during an experimental run complicates the calculations involved but yields more reliable information for practical operation and design. In drying leather it is important to hang it in vertical sheets and to pass the air downward over the vertical surfaces rather than to blow the air horizontally. This is necessary because of the irregular shape and size of skins. If air were passed horizontally, the stream would channel through the open spaces of the bottom end without effective contact with the surface. In a progressive drier for leather, air should be passed in a helical spiral through the drier, winding its way countercurrent to the travel of the stock, the air passing downward through the sheets of leather, leaving at the bottom, and bypassing through side channels to the top of the next group of skins. Fans must be provided to effect each turn of the air stream, to maintain a helical flow, and to avoid a horizontal flow.

A diagram of the experimental drier is shown in Figure 2.

The temperature of the air entering the leather was controlled by automatic regulation of the steam supply to the heating coil by means of a Johnson thermoregulator. Each skin was hung from four supports with the butt ends up and adjustable to different spacings. A distance of 5 cm. apart was the minimum value found necessary to avoid touching and to allow a free passage of air. Fresh air was admitted through a port in the side. The proportion of fresh air admitted could be adjusted by varying the size of these port openings. A special intake at the front permitted admission of higher proportions of fresh air. Air was circulated by means of a blower and the rate of flow varied by changing the pulley ratios on the drive shaft. A continuous printed record of dry- and wet-bulb temperatures was registered by means of a Foxboro recording psychrometer. The leather was suspended on hooks fastened to a wooden frame, the whole of which was suspended from a platform scale mounted above the drier. By this scale a continuous record of the weight of leather and its moisture content could be obtained for the entire run.

Wet- and dry-bulb thermometers, precise to 0.1° C., were placed for measuring the temperatures of fresh, spent, and recirculated air. The final moisture content of the leather after drying was obtained by cutting off samples for chemical analysis. Such samples were taken from various parts of the skin to determine uniformity of drying and the average moisture content. The humidity of air was controlled by regulating the supply of fresh air and also by admission of steam at the beginning of the run. The fact that the drier was constructed of wood interfered with humidity control but did not affect the experimental values of drying coefficients. The velocity of air flowing downward between the skins was measured by an anemometer. Readings were taken at twenty-one different points at a horizontal elevation halfway down the skins. These velocities varied greatly from point to point owing to the irregularity of leather. From fifteen to thirty skins were taken for each test immediately after the operation of hand-setting.

The following variations in drying conditions were tested:

Average air velocities, 14 to 142 kg. per square meter per minute
Temperature of saturated air, 26° to 60° C.
Temperature of dry air, 26° to 93° C.
Initial moisture content of leather, average 1.5 kg. per kg. of dry leather (60 per cent water)
Final moisture content of leather, 0.025 to 0.155 kg. per kg. of dry leather (2.4 to 13.4 per cent water)
Fraction of water removed, 90 to 98.5 per cent
Time of drying, 2.5 to 18 hours
Average thickness of stock, calfskins 1.03 mm., kips 1.4 mm.
Average density of leather excluding water, before drying 0.46, after drying 0.50

After drying, the thickness of each skin was measured at five different places—namely, in the head, right butt, left butt, right brisket, and left brisket. The stock was placed "in crust" for at least 12 hours. The dried leather was then dipped in water for 10 minutes. After dipping, the skins were passed through the normal operations of sammying, staking, tacking, trimming, graining, and seasoning. Shrinkage of leather in drying was determined by measuring the area after hand-setting and after tacking. All area measurements were made by the same operator and on the same machine. The average shrinkage in area during drying was 5.7 per cent.

Drying experiments were conducted under different conditions in order to ascertain the variation of the drying coefficient, B, with the variable factors such as temperature, air velocity, thickness of stock, and spacing of skins. Temperature readings of dry- and wet-bulb thermometers of the fresh, recirculated, and spent air were taken in duplicate every 10 minutes. To compensate for fluctuations in temperature due to operation of the thermoregulator, the temperature readings were taken in duplicate at half-cycle intervals of the periodic operation of heater. For instance, if the thermoregulator operated every 2 minutes, readings were taken 1 minute apart for each 10-minute interval. Average of duplicate readings were used in calculations. The period of fluctuation increased as the leather approached dryness. The weight of leather was also recorded at 10-minute intervals.

In starting a test the drier was first heated to the desired temperature, and the air was saturated by blowing in live steam. All outside ports were closed, and air was recirculated for 15 minutes. A regulated fraction of fresh air was admitted and the drying was continued until the leather reached a constant weight.

A complete log of data for run 16 is given in Tables I, II, and III. Velocities were not recorded for this run.

TABLE I. EXPERIMENTAL DATA FOR RUN 16

(Stock, 30 L M calfskins; temperature of air entering above leather, 49° C.; time of drying, 3 hours 50 minutes; spacing, 2.5 cm. apart)

	WEIGHT OF STOCK	MOISTURE CONTENT PER KG. DRY STOCK, T		THICKNESS AFTER DRYING
	Kg.	*Kg.*		*Mm.*
After hand-setting	34.5	1.52	Shoulder	1.04
After drying, average	15.4	0.118	Right brisket	0.89
In butt	..	0.117	Left brisket	0.86
In belly	..	0.122	Right butt	1.07
In shoulder	..	0.121	Left butt	1.02
In crust	15.9	0.154	Average	0.98
In sammying	25.5	0.852		
Bone-dry	13.8	0.0		

TABLE II. EXPERIMENTAL DATA FOR RUN 16

TIME	WEIGHT OF STOCK	WEIGHT OF WATER	TEMPERATURE: FRESH AIR Dry	TEMPERATURE: FRESH AIR Wet	TEMPERATURE: RECIRCULATED AIR Dry	TEMPERATURE: RECIRCULATED AIR Wet	TEMPERATURE: SPENT AIR Dry	TEMPERATURE: SPENT AIR Wet
Min.	*Kg.*	*Kg.*	*° C.*	*° C.*	*° C.*	*° C.*	*° C.*	*° C.*
0	34.2	20.4	..	..	51.2	48.1	50.8	47.6
5	33.8	20.0	..	..	49.5	45.8	49.2	45.7
10	33.4	19.6	..	..	48.3	44.4	48.0	44.5
15	33.0	19.3	..	..	48.1	43.5	47.4	43.8
20	32.6	18.8	..	..	48.9	44.2	47.8	44.2
25	32.2	18.4	..	..	49.7	44.4	48.2	44.3
30	31.8	18.0	..	..	49.0	43.0	48.2	42.1
40	30.5	16.8	..	..	49.0	42.8	48.2	42.8
50	29.2	15.4	31.1	21.1	49.6	40.5	48.6	41.3
60	27.9	14.0	30.9	22.8	49.4	40.0	49.0	40.3
70	26.2	12.4	..	..	49.7	39.6	48.9	39.8
80	25.1	11.3	31.0	22.2	49.7	39.0	49.2	39.4
90	23.9	10.1	31.7	22.4	49.9	38.4	48.9	38.7
100	22.7	8.9	..	..	49.5	37.6	48.7	37.8
120	21.7	6.85	30.6	21.2	48.3	35.6	47.8	36.1
130	19.8	5.95	..	..	49.0	35.1	48.1	35.6
140	19.1	5.3	31.8	21.6	49.4	34.4	48.2	35.0
150	18.4	4.6	..	..	49.1	33.6	47.9	33.2
160	17.9	4.1	31.7	21.3	49.1	32.8	47.9	33.4
170	17.3	3.5	..	..	48.9	32.2	48.1	32.8
180	16.7	3.0	..	..	49.0	31.7	48.1	32.3
190	16.4	2.5	..	..	49.3	30.7	48.1	31.3
200	16.1	2.3	30.9	19.7	47.8	29.4	47.2	30.2
210	15.9	2.1	..	..	48.4	28.9	47.7	30.0
220	15.6	1.8	..	..	48.8	28.5	48.0	29.7
230	15.4	1.6	..	..	48.5	28.0	47.6	29.2

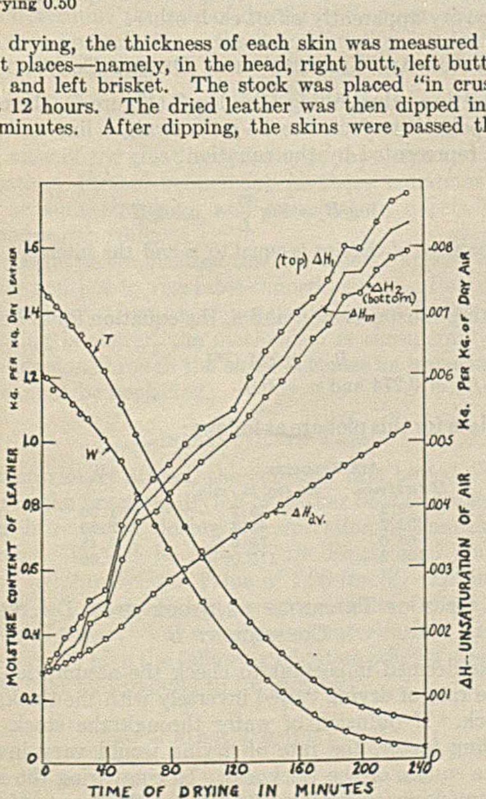


FIGURE 3. EXPERIMENTAL DATA FOR RUN 16

Thickness of stock, 0.98 mm.; temperature, 120° F. (48.9° C.)

In Figure 3 the following experimental values were plotted against time: total moisture content, free moisture content, unsaturation of air entering above the skin, and unsaturation of air leaving below the skin. Since the change in unsaturation of air in passing once over a single skin is slight, the mean unsaturation in the drier at any instant, ΔH_m, was taken as the arithmetic mean of the entering and leaving values. This mean value was also plotted. The average integrated value of the unsaturation of air over any elapsed period of time, $\Delta H_{av.}$, was obtained by graphical integration of the equation:

Table III. Calculated Data for Run 16

Time	Recirculated Air		Spent Air	Unsaturation of Air $(H_w - H)10^3$									Average in Drier		
θ	t	$t - t_w$*	$t - t_w$	Recirculated, ΔH_1	Spent, ΔH_2	Mean ΔH_m	ΔH_1 for time interval	$\Delta H_{Av.}$ for time elapsed	T	E	W	$\theta \Delta H_{av.}$	t	$t - t_w$	Relative humidity
Min.	° *C.*	° *C.*	° *C.*	*Kilograms per kilogram of dry air*											
0	51.2	3.2	3.2	1.355	1.355	1.355	..	..	1.48	0.27	1.21	0	51.0	3.2	83
5	49.6	3.8	3.45	1.62	1.45	1.52	1.44	1.44	1.45	0.255	1.195	7.2	48.9	3.7	80
10	48.3	3.9	3.45	1.665	1.475	1.57	1.545	1.49	1.42	0.257	1.161	14.9	48.1	3.7	80
15	48.1	4.5	3.8	1.93	1.545	1.74	1.655	1.55	1.39	0.25	1.14	23.2	47.7	4.05	79
20	48.9	4.85	3.7	2.07	1.57	1.82	1.78	1.605	1.36	0.248	1.112	32	48.3	4.25	78
25	48.9	5.3	3.8	2.26	1.64	1.95	1.885	1.66	1.33	0.245	1.085	41.5	48.9	4.55	77
30	49.8	5.9	5.1	2.52	2.19	2.34	2.195	1.75	1.30	0.23	1.07	52.5	48.6	5.5	72
40	48.9	6.2	5.3	2.64	2.28	2.46	2.40	1.91	1.22	0.215	1.021	76.5	48.6	5.75	71
50	49.6	8.55	7.3	3.67	3.12	3.40	2.93	2.12	1.114	0.178	0.936	106	49.0	7.95	62
60	48.9	9.5	8.7	4.07	3.74	3.905	3.65	2.37	1.015	0.185	0.830	142	49.1	7.9	61
70	49.8	10.2	9.0	4.38	3.86	4.12	4.01	2.61	0.897	0.17	0.727	182.5	49.3	9.6	56
80	49.7	10.8	9.8	4.62	4.19	4.405	4.26	2.81	0.819	0.158	0.661	225	49.4	10.5	52.5
90	49.9	11.5	10.3	4.93	4.41	4.67	4.54	3.01	0.733	0.155	0.572	270	49.4	10.9	50
100	49.5	12.0	10.8	5.14	4.64	4.89	4.78	3.18	0.646	0.150	0.496	318	49.1	11.4	48
120	48.3	12.7	11.7	5.45	5.03	5.24	5.065	3.50	0.496	0.14	0.356	420	48.1	12.2	44.5
130	48.9	13.9	12.5	5.95	5.35	5.65	5.445	3.64	0.431	0.13	0.301	473	48.5	13.2	41
140	49.4	14.9	13.2	6.37	5.64	6.005	5.83	3.80	0.384	0.13	0.254	532	48.8	14.0	39.5
150	49.1	15.5	13.7	6.65	5.88	6.265	6.135	3.96	0.332	0.122	0.217	594	48.6	14.6	37
160	49.0	16.3	14.5	6.96	6.21	6.58	6.42	4.11	0.296	0.115	0.181	656	48.5	15.4	35
170	48.9	16.8	15.3	7.19	6.55	6.87	6.725	4.26	0.245	0.11	0.135	723	48.4	16.0	32.5
180	49.0	17.3	15.8	7.43	6.74	7.095	6.98	4.42	0.214	0.105	0.109	794	48.5	16.6	30.5
190	49.2	18.6	16.8	7.98	7.20	7.59	7.34	4.57	0.184	0.10	0.084	869	48.7	17.7	28
200	47.8	18.4	17.0	7.90	7.25	7.555	7.57	4.72	0.164	0.10	0.064	944	47.6	17.7	27
210	48.4	19.5	17.7	8.35	7.60	7.98	7.77	4.87	0.148	0.092	0.056	1020	48.1	18.6	25
220	48.8	20.3	18.3	8.68	7.80	8.76	8.37	5.02	0.132	0.09	0.042	1100	48.3	19.3	25
230	48.5	20.6	18.4	8.80	7.88	8.34	8.55	5.17	0.118	0.085	0.033	1190	48.0	20.0	22

* t = dry-bulb temperature; t_w = wet-bulb temperature.

$$\frac{\int_0^\Theta \Delta H_m \, d\Theta}{\Theta}$$

where $$\Delta H_m = \frac{\Delta H_1 + \Delta H_2}{2}$$

These values are also plotted in Figure 3. Knowing the average integrated value of unsaturation, Equation 1 becomes:

$$\frac{dW}{W} = -B \Delta H_{av.} \, d\Theta \tag{4}$$

Upon integration, this becomes:

$$\ln \frac{W_0}{W_1} = B \Delta H_{av.} \, \Theta \tag{5}$$

Instead of calculating B for each value of Θ, an average value for the entire run was obtained graphically. Values of log W were plotted against $\Theta \Delta H_{av.}$ (Figure 4).

Table IV. Summary of Experimental Data on Drying Coefficients

Run	Drying Temp.	Time of Run	Air Velocity	Av. Thickness, L	Moisture Content Before drying	Moisture Content After drying	Area Shrinkage in Drying	Drying Coefficient, B
	° *C.*	*Hrs.*	*Kg./sq. m./min.*	*Mm.*	%	%	%	
1	26–49	19	14.1	1.05	61.9	11.5	8.6	1.305
4	49	3.5	42.7	1.17	60.4	13.1	9.0	1.90
5	55	2.7	42.0	1.06	60.5	10.3	9.1	2.71
6	51	3.5	42.5	1.00	60.9	13.5	7.2	2.61
7	43–49	6.2	42.3	1.04	60.7	11.4	6.3	2.48
8	49	4.7	71.4	1.13	61.0	9.0	7.3	3.61
9	54	3.7	70.0	1.02	61.7	9.5	10.3	3.48
10	43–54	3.0	71.4	0.98	55.5	9.7	8.2	3.35
11	49	3.2	117.0	1.02	59.9	11.3	7.4	4.95
13	54	3.5	115	1.00	62.0	9.9	8.8	4.38
15	60	3.5	112	1.06	63.8	8.8	7.6	4.63
16	49	3.6	98.8	0.98	60.4	10.6	3.6	3.11
22	32	2.5	124	..	55.5	35.6	3.5	4.67
28	54	2.5	114	1.04	61.6	11.5	3.6	4.65
17	49	5.0	99.6	1.32	62.0	10.1	3.3	3.18
30	54	4.5	99.6	1.43	59.5	8.4	5.7	3.55

The deviation of points from a straight line is well within the range of experimental error. This indicates that the proposed theory of drying and the rate of drying expressed by Equation 4 is substantially sound and reliable. The slope of the straight line in Figure 4 multiplied by 2.303 represents the average value of the drying coefficient, B, for run 16 and is equal to 3.11. A summary of experimental data for all runs is given in Table IV.

Effect of Air Temperature

Variations in temperature affect the diffusion coefficient of vapor and also the viscosity of air, and hence it would be expected that values of m in Equation 2 would also be affected by temperature. However, by plotting values of B for constant values of air velocity and thickness of stock, it is seen (Figure 5) that the temperature effect is negligible over the rather limited range of temperatures employed in these experiments. The effects of temperature upon diffusivity and viscosity apparently offset each other.

Effect of Air Velocity upon Drying Coefficient

By plotting values of log V *vs.* log G (Figure 6), the experimental points are found to lie on a straight line and hence may be represented by the equation:

$$\log B = \log \frac{m}{L} + \text{n} \log G$$

where the slope of the line is equal to n and the intercept to log m/L.

Evaluating constants m/L and n, the equation for B becomes

$$B = 0.274 \, G^{0.6} \tag{6}$$

where $m/L = 0.274$ and $n = 0.6$

The data for this plot are as follows:

Air Velocity		B
Meters/min.	*Kg./sq. m./min.*	
12.2	13.7	1.30
39.7	42.4	2.60
66.0	70.9	3.48
108.2	115.0	4.66

Effect of Thickness of Stock upon Drying Coefficient B

It was deemed important to check the assumption made that the rate of drying varied inversely with the thickness of the stock. If diffusion of water through the stock was a controlling factor, the rate of drying would vary inversely with the square of the thickness. In comparing the rate of drying calfskins (thickness, 1.03 mm.) with the rate of drying kips (thickness, 1.37 mm.) at the same air velocity, the following values were obtained:

Thickness Mm.	B	m/L	m
1.03	4.34	0.274	0.282
1.37	3.36	0.212	0.290

Within the limits of experimental error it was concluded that the drying coefficient, B, varies inversely with thickness as assumed earlier, and that resistance to diffusion through the stock is a negligible factor. The shrinkage of leather during drying did not seem to alter appreciably the drying coefficient.

Final Equation

The final equation for the rate of drying chrome leather becomes:

$$\frac{dW}{d\Theta} = -\frac{0.282}{L} G^{0.60} W \Delta H \qquad (7)$$

where W = free moisture content, kg. of water per kg. of dry stock
L = thickness of leather, mm.
G = mass velocity of air, kg. of air-vapor mixture per square meter per minute
Θ = time elapsed, minutes
ΔH = unsaturation of air = $H_w - H$
H_w = humidity of air at wet-bulb temperature, kg. per kg. of dry air
H = humidity of air in main air stream

Equation 7 is suitable for the air-drying of chrome leather when the air flows vertically downward over and between vertical sheets of leather spaced 2.5 cm. or more apart and for values of air velocity, G, above 10 kg. per square meter per hour, and for values of moisture content below 60 per cent, ($T = 1.5$).

For drying leather in still air, it will be safe to use the equation:

$$\frac{dW}{d\Theta} = -\frac{1.12}{L} W \Delta H \qquad (8)$$

To determine the rate of drying leather per square meter of surface on each side of the skin, Equation 7 reduces to:

$$\frac{dW}{Ad\Theta} = -0.065\, G^{0.6}\, W \Delta H \qquad (9)$$

In view of the great irregularity in the shape and thickness of leather, further refinement in these equations to take into account shrinkage and temperature effects were not deemed worth while.

It should be emphasized that Equation 7 applies to chrome leather and not to vegetable-tanned leather. Because of the much denser structure of vegetable-tanned leather the rate of drying is slower, the mechanism is considerably altered, and diffusion through the stock becomes an important factor and cannot be neglected.

Constant Rate Period

As previously stated, the constant rate period should not occur in the practical drying of leather because excess surface water is removed during the operation of hand-setting by scraping. It will be safe to use Equation 7 during this period by employing a value of 1.25 for W. Drying during this period is equivalent to evaporation from a vertical surface of water. For a horizontal water surface, Himus and Hinchley (*1*) give the following equation when a stream of air passes over and parallel to the surface:

$$\frac{dW}{Ad\Theta} = (0.031 + 0.0135V)\, \Delta P \qquad (10)$$

where V = velocity of air, meters per second
W = water, kg.
A = surface, square meters
Θ = time elapsed, hours
ΔP = $P - p_d$
P = vapor pressure of water at surface, mm. of mercury
p_d = vapor pressure of water at dew point of air, mm. of mercury

Equation 10 holds for values of V from 0.5 to 4.0 meters per second and at atmospheric pressure.

Reducing Equation 9 to the same units for the constant rate period, there results:

$$\frac{dW}{Ad\Theta} = 0.057V^{0.6}\, \Delta P \qquad (11)$$

Over the velocity range in question this latter equation is about 40 per cent higher than the data of Himus and Hinchley. This difference is reasonable since it is to be expected that the rate of evaporation of water from a vertical liquid surface will be greater than from a horizontal surface.

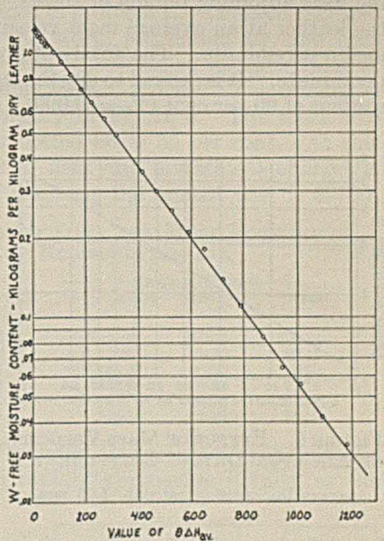


Figure 4. Evaluation of Drying Coefficient B in Run 16

Thickness, 0.98 mm.; temperature, 120° F. (48.9° C.)

Application of Drying Equation

An accurate knowledge of drying coefficients is useful in problems dealing with the design of driers and especially in calculating the most economical conditions of operation. The fact that successful design and operation are accomplished without such information is because ordinarily the operating conditions of a drier are extremely flexible as to time, temperature, recirculation, and air velocity, so that any shortcoming of the drier may be readily corrected by altering these conditions. However, the most economical design and most economical method of operation can be calculated only from a knowledge of such coefficients. The method of applying these coefficients will be demonstrated for three types of problems dealing with the use of a progressive drier for drying chrome leather. It is desired to calculate: (1) the time required for drying and the corresponding length of drier, (2) the optimum velocity at which air should be passed over the sheets of leather, and (3) the most economical fraction of air to recirculate.

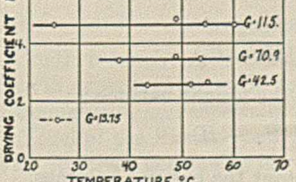


Figure 5. Effect of Temperature of Air upon Drying Coefficient B

Assume the following general problem in the drying of leather: It is desired to dry 10,000 calfskins per 24 hours in a progressive drier operating continuously for 300 days in the year. The skins are to be suspended vertically 6.3 cm. apart and placed parallel to the direction of travel. The drier is of such dimensions as to accommodate 28.2 skins per meter of length. The average thickness of skin is 1.03 mm., the average dry weight is 0.527 kg., the average initial moisture content is 1.562 kg. per kg. of dry leather. Air enters the preheater at 26.6° C. (80° F.) and 70 per cent relative humidity at atmospheric pressure, and is heated to 60° C. (140° F.) before entering the drier. The air passes in a helical stream through the drier, flowing downward through the vertical sheets of leather and by-passing through a side channel to the next adjoining bundle of sheets. The air flows through the leather at an average mass velocity of 39 kg. per square meter per minute. The total supply of dry air is 390 kg. per minute. It is desired to dry the leather to a final moisture content of 90 per cent ($T_1 = 0.099$).

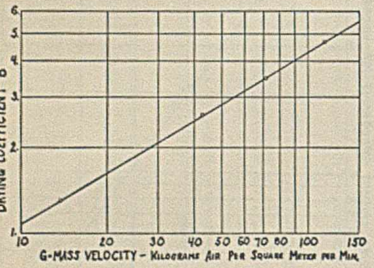


FIGURE 6. EFFECT OF MASS VELOCITY OF AIR UPON DRYING COEFFICIENT B

Average thickness of calfskin, 1.03 mm.

The cost of tunnel construction not including fans is $164 per meter of length. The cost of steam is $1.98 per million Calories, and the cost of power is 2.7 cents per kilowatt-hour. The annual charge for interest, depreciation, and taxes on all investment costs is 25 per cent.

The symbols used in these problems have the same significance as previously defined. Subscript 0 refers to conditions at the end of drier where the leather enters and subscript 1 to conditions at the other end where the leather leaves:

t = dry-bulb temperature, ° C.
t_w = wet-bulb temperature, ° C.
r = ratio of dry air to dry stock per unit time

For this particular problem the general drying equation (7) becomes:

$$\frac{dW}{d\Theta} = -2.46\, W \Delta H \qquad (12)$$

Direct integration of this equation is not possible because the relationship between free moisture content, W, and humidity, H, cannot be expressed by any simple formula. In a progressive drier the temperature and humidity of the air vary progressively from one end of the drier to the other, and also the conditions of the stock as to temperature and total, free, and equilibrium moisture contents vary progressively from entrance to exit. The water balance of the drier is given by the equation:

$$T_0 - T_1 = r\,(H_0 - H_1)$$

For any given length of drier the weight balance is:

$$T_0 - T = r\,(H_0 - H)$$

In terms of free moisture content the balance becomes:

$$(W_0 + E_0) - (W + E) = r\,(H_0 - H)$$

Since E varies progressively through the drier and depends upon a complicated relation to temperature and relative humidity, as shown in Figure 1, it becomes evident that a mathematical integration of Equation 12 becomes impossible. For the special case of countercurrent driers where ΔH remains nearly constant, the equation integrates to the form:

$$\ln \frac{W_0}{W_1} = -2.46\,(\Delta H)_{\text{av.}}\,\Theta$$

PROBLEM 1. DRYING TIME AND LENGTH OF DRIER

Assume that the air is maintained at a constant temperature of 60° C. throughout the drier. This can be accomplished by distributing heating coils in the side channels along the entire length of drier so that each time the air stream has passed over a sheet of leather, the heater restores its temperature to 60° C. To solve Equation 12 by graphical integration requires a knowledge of conditions at every point in the drier. Assuming any given value of total moisture content, T, the corresponding humidity of air can be found from the weight balance:

$$T_0 - T = r(H_0 - H) \text{ or } 1.562 - T = 106\,(0.0296 - H)$$

Knowing the humidity, H, and the dry-bulb temperature, 60° C., the relative humidity and wet-bulb temperature of the air can now be obtained from a standard psychrometric chart. If the Grosvenor chart is used, it is first necessary to convert relative humidities to percentage humidities. Knowing the temperature and relative humidity of the air, the equilibrium moisture content of the leather, E, can be obtained from the chart of equilibrium moisture content (Figure 1). The free moisture content follows from the relation, $W = T - E$. The humidity of air at the wet-bulb temperature can be obtained from the psychrometric chart. The unsaturation of the air is found from the equation $\Delta H = H_w - H$ or can be calculated from the relationship $\Delta H = 0.000429\,(t - t_w)$. Values of $1/W\Delta H$ are calculated for each assumed value of T. Equation 12 can now be integrated by plotting values of $1/W\Delta H$ against W and integrating graphically between the limits W_0 and W_1. Typical calculations are given in Table V. The value of the integral is 300 units. Hence,

$$\Theta = \frac{300}{2.46} = 122 \text{ minutes}$$

Since in this particular problem the value of ΔH varies but slightly through the entire drier, an alternative solution may be used. By using an average value of $\Delta H = 0\ 0116$, Equation 12 can be directly integrated and becomes:

$$\ln \frac{W_0}{W_1} = 2.46 \times 0.0116 \times \Theta$$

Solving for known values of W_1, Θ becomes 120 minutes.

Since the output of the drier is 3.69 kg. of dry leather per minute, the capacity of the drier must be 3.69 × 122 = 445 kg. The weight of dry leather per meter of drier is 14.83 kg. Hence the required length of drier must be 30 meters.

TABLE V. CALCULATED DATA FOR GRAPHICAL INTEGRATION

T	H	t_w ° C.	RELATIVE HUMIDITY	H_w	ΔH	E	W	$\frac{1}{W\Delta H}$
1.562	0.0296	36.4	23	0.0397	0.0101	0.078	1.484	67
1.4	0.0281	35.9	22	0.0385	0.0104	0.075	1.325	72
1.2	0.0262	35.0	20	0.0369	0.0107	0.070	1.13	83
1.0	0.0243	34.2	19	0.0354	0.0111	0.068	0.932	97
0.8	0.0224	33.7	18	0.0339	0.0115	0.065	0.735	118
0.6	0.0205	32.8	17	0.0322	0.0117	0.060	0.540	161
0.4	0.0187	32.0	16	0.0307	0.0120	0.058	0.342	244
0.2	0.0168	31.1	14	0.0292	0.0124	0.052	0.148	555
0.099	0.0158	30.6	13	0.0289	0.0131	0.050	0.049	1610

ADIABATIC DRYING. If the same leather were to be dried adiabatically with air entering at 60° C., the same procedure would be followed. In this case the wet-bulb temperature would remain constant at 30.6° C., and from a knowledge of humidity the values of dry-bulb temperature and relative humidity are obtained from the psychrometric chart. In solving this particular problem for adiabatic drying, it will be found that $H_0 = 0.0296$ and $H_{w0} = 0.0289$; hence ΔH_0 becomes negative. This means that for the given conditions the air becomes saturated before drying is complete; hence adiabatic drying is impossible for the stated conditions. In order to dry adiabatically, it would be necessary either to increase the temperature of the entering air or increase the velocity of air flow.

Problem 2. Optimum Air Velocity through Leather

As the velocity of air passing through the leather is increased, the length of drier may be shortened; this results in a saving in the cost of drier and also reduces the cost of heat losses through the walls of the drier. On the other hand, as air velocity is increased, the cost of power for blowing air and the investment cost of blowers will increase. Obviously the optimum velocity will be obtained when the total cost becomes a minimum. To determine this optimum velocity, it will be necessary to assume a series of values of G and for each value to calculate the corresponding length of drier required as described in problem 1.

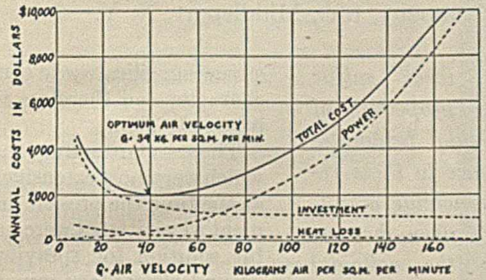


Figure 7. Effect of Velocity of Air upon Annual Costs

For a particular well-insulated drier the heat losses are 500 Calories per hour per meter of length. The power costs and size of blower can be obtained from the pressure required to blow the air through the leather and heater coils, including all bends, contractions, and expansions. With cost of heat $1.98 per million Calories, cost of power 2.7 cents per kilowatt-hour, and an annual charge of 25 per cent for interest, overhead, and taxes on all investment costs, the results shown in Figure 7 and Table VI were obtained. The optimum velocity of air is 39 kg. per square meter per minute. These calculations apply to a progressive drier operating at a constant temperature of 60° C. with no recirculation of air.

Table VI. Calculated Data for Optimum Air Velocity

G'	G	Θ	Length	Annual Costs: Investment, drier, fans	Annual Costs: Radiation	Annual Costs: Power	Annual Costs: Total
Lb./sq. ft./min.	*Kg./sq. m./min.*	*Min.*	*Meters*				
2	9.8	348	86	$3736	$615	$44	$4395
4	19.6	200	49.4	2270	354	86	2710
8	39.2	122	29.8	1525	214	316	2055
12	58.6	96	23.8	1328	170	820	2318
16	78.2	76	18.7	1139	134	1470	2743
20	97.6	67	16.5	1080	118	2560	3758
24	117	60	14.8	1044	106	3900	5050
28	137	54	13.4	1012	96	5680	6788
32	156	49.5	12.2	982	87	7640	8709
36	176	46	11.3	962	81	10300	11243
40	196	43	10.7	962	76	13200	14238

Problem 3. Most Economical Fraction of Recirculated Air

In the particular problem illustrated for drying at a constant temperature of 60° C. (140° F.) and at an optimum air velocity of 39 kg. per square meter per minute, the air leaves the drier at a relative humidity of only 23 per cent. It is reasonable to believe that operation costs could be reduced by recirculating a fraction of the air. As the fraction of recirculated air is increased, the length of drier must be increased with a corresponding increase in cost of drier and cost of heat lost through the walls. On the other hand, with an increase in fraction of circulated air the amount of fresh air will be reduced, and a corresponding decrease in heat required for preheating air will be obtained. Letting x equal the fraction of air recirculated and h_1 equal the humidity of fresh air the following weight balances will be obtained:

$$T_0 - T_1 = r\,(H_0 - H_1)$$

$$T_0 - T_1 = r\,(1 - x)\,(H_0 - h_1) \qquad (13)$$

The length of drier is calculated for a series of values of x in the same manner as outlined in problem 1. The heat required for evaporation, preheating stock, preheating air, and heat losses through drier can then be calculated for each value of x and for the corresponding length of drier. The calculated results are shown graphically in Figure 8. The most economical fraction of recirculated air is 55 per cent. At this fraction the annual cost of heat and investment charges is $7600, whereas with all fresh air the annual cost is $9700.

Table VII. Calculated Data for Most Economical Fraction of Recirculated Air

x	Θ	Length	Annual Costs: Investment	Annual Costs: Heat	Annual Costs: Total
	Min.	*Meters*			
0	122	30	$1231	$8500	$9731
0.2	131	32.3	1325	7420	8745
0.4	159	39.4	1612	6400	8012
0.5	186	45.8	1875	5850	7725
0 55	197	48.5	1987	5650	7637
0.6	246	60.6	2490	5450	7940

As the fraction of recirculated air exceeds 55 per cent, the length of drier required rapidly approaches infinity as the equilibrium moisture content of 0.099 is reached and costs rise accordingly.

In order to reduce leather to a moisture content of $T = 0.099$ with air drying at 60° C., the relative humidity of the entering air cannot be increased above 32 per cent (Figure 1); the corresponding humidity of the entering air $H_1 = 0.0428$ and from the weight balance H_0 is found to be 0.0565. Substituting these values in Equation 13, we obtain:

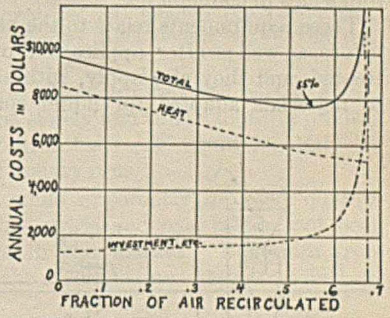


Figure 8. Effect of Recirculation of Air upon Drying Costs

$$1.562 - 0.099 = 106\,(1 - x)\,(0.0565 - 0.0158) \text{ or } x = 0.66$$

The maximum fraction of recirculated air is then 66 per cent. A larger percentage will result in inadequate drying.

Acknowledgment

Credit is hereby acknowledged to Peter Wenck for assistance in experimental work, to N. H. Ceaglske for correction of manuscript, and especially to Fred Vogel, Jr., and Charles P. Vogel of the Pfister-Vogel Leather Company, Milwaukee, Wis., for their generosity in releasing the experimental data presented in this paper. These particular experiments were performed by the author in 1926 in the laboratories and plant of the Pfister-Vogel Leather Company. Since then much advance has been made in the general theory of drying, but the author has found no justification for altering his interpretation of the experimental data on the drying of chrome leather.

Literature Cited

(1) Himus and Hinchley, J. W., *Chemistry & Industry*, 43, 840 (1924).
(2) McCready, D. W., and McCabe, W. L., *Trans. Am. Inst. Chem. Engrs.*, in press (1933).
(3) Newman, A. B., *Ibid.*, 27, 203, 310 (1931).
(4) Sherwood, T. K., Ind. Eng. Chem., 21, 12, 976 (1929).
(5) *Ibid.*, 24, 307 (1932).
(6) Walker, Lewis, and McAdams, "Principles of Chemical Engineering," 2nd ed., pp. 457, 516, McGraw-Hill, 1927.

Received August 26, 1933.

Colloidal Bentonite-Sulfur

A New Fungicide

A. S. McDaniel, Niagara Sprayer and Chemical Company, Inc., Middleport, N. Y.

The essential requisites of an "ideal" sulfur fungicide are outlined, and the properties of the new product, known as colloidal bentonite-sulfur, are discussed with reference to these requirements. The method of commercial manufacture is described, and data are given showing the close resemblance between the colloidal properties of the new product and those of bentonite itself. Data on toxicity by the spore count method and on the commercial control of a typical orchard fruit disease are presented.

THE primary requisites of an entirely satisfactory or "ideal" sulfur fungicide for agricultural uses can be stated to comprise the following: (1) safety to the growing plant; (2) high toxicity to the disease organism; (3) high degree of adhesiveness under adverse weather conditions; (4) wettability or dispersibility in water; (5) low cost per control unit or dose; (6) convenience in use; (7) stability and uniformity under normal conditions; (8) compatibility with other classes or types of insecticides and fungicides in common use.

These requirements relate to the properties of the material before, as well as after, application to the growing plant to be treated, and they also apply, with almost equal pertinency, to materials adapted for liquid spraying or dry dusting.

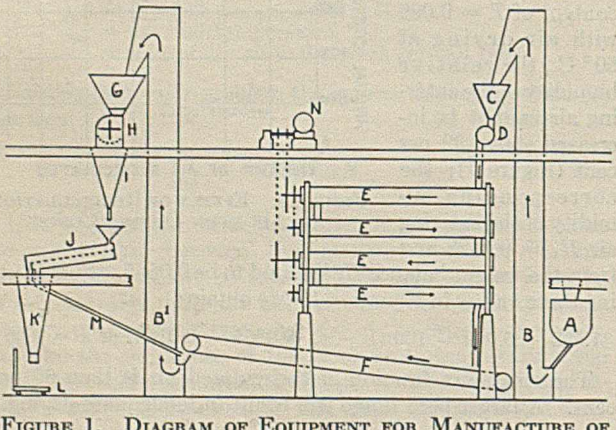


Figure 1. Diagram of Equipment for Manufacture of Kolobase

The fundamental and most difficult problem to be considered in the development of a new fungicide is unquestionably the provision of a material which combines a wide margin of safety to the plant with a high degree of toxicity toward the fungous or disease organism, and the difficult nature of the problem lies in the fact that these two properties are diametrically opposed to each other.

A further problem of almost equal difficulty is the provision of a product possessing the desired degree of adhesiveness and wettability. These properties, like toxicity and safety, are also inherently opposed to each other and cannot often be combined in one and the same material or mixture. This is due, in large part at least, to the fact that most adhesives or stickers, which are otherwise suitable, are reversible colloids in nature and tend to wash off under adverse weather conditions. Incidentally, with few exceptions, the adhesives proposed for this purpose, such as animal glue, casein, and the like, possess nutrient properties with respect to fungi and bacteria in general, and are therefore objectionable; those which do not have this objectionable characteristic, such as sodium silicate, are caustic in character and therefore tend to injure the plant.

The standard sulfur fungicides which were most extensively used at the time the present development was initiated were lime sulfur solution for spraying, and ground elementary mineral sulfur for dusting. These materials were believed to be seriously defective with reference to certain of the fundamental requirements outlined above. Thus, lime sulfur solution is seriously lacking in safety and chemical stability, although highly toxic to the group of fungous diseases known to be susceptible to sulfur materials. The inconvenience and expense to the manufacturer in packing and shipping and to the user in handling and mixing a somewhat noxious and chemically active liquid of this nature, as distinguished from a stable solid, is also objectionable.

On the other hand, ground mineral sulfur dust, which was developed partly for the purpose of overcoming these objectionable characteristics of lime sulfur solution and partly in order to take advantage of the greater speed and convenience of the dusting method, was considered lacking in toxicity, adhesiveness, spreadability, etc. Improvement of ground sulfur dusts in these respects was therefore considered desirable.

General Statement of Results

In recent years, however, important advances have been made in approaching more nearly to this desired goal, and it is the purpose of this paper to discuss certain aspects of one of these recent developments represented by a highly colloidal product made from bentonite and molten sulfur, now generally known in the insecticide and fungicide industry as colloidal bentonite-sulfur. It is marketed in the pure form for liquid spray use under the trade name of Kolofog, and in various combinations with other fungicides and insecticides for both spraying and dusting under the trade names of Koloform, Kolodust, Kolotex, etc.

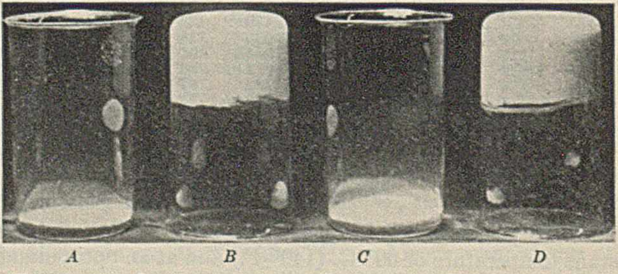


Figure 2. Illustration of Gelatinous Properties of Bentonite and of Bentonite-Sulfur

A. Powdered bentonite-sulfur
B. Bentonite-sulfur gel (6 parts water)
C. Powdered bentonite
D. Bentonite gel (6 parts water)

Briefly stated, the new product is made by absorbing molten sulfur into dry, ground bentonite clay and permitting the molten sulfur to solidify *in situ* in the dry bentonite. A mere mechanical mixture of sulfur and bentonite does not give a product possessing the desired properties. The details of the commercial method of manufacturing the new product are described later. The new product and various methods of production are patented (*2*), and commercial production and distribution are conducted under an exclusive license under the patents mentioned.

Colloidal bentonite-sulfur was first produced and marketed on a commercial scale in 1925 and immediately met with favorable reception by fruit growers generally.

An interesting incident of the commercial development of this new fungicide is the fact that the utilization of colloidal bentonite in connection with the manufacture of the finished product now represents one of the most important commercial uses of bentonite clay itself.

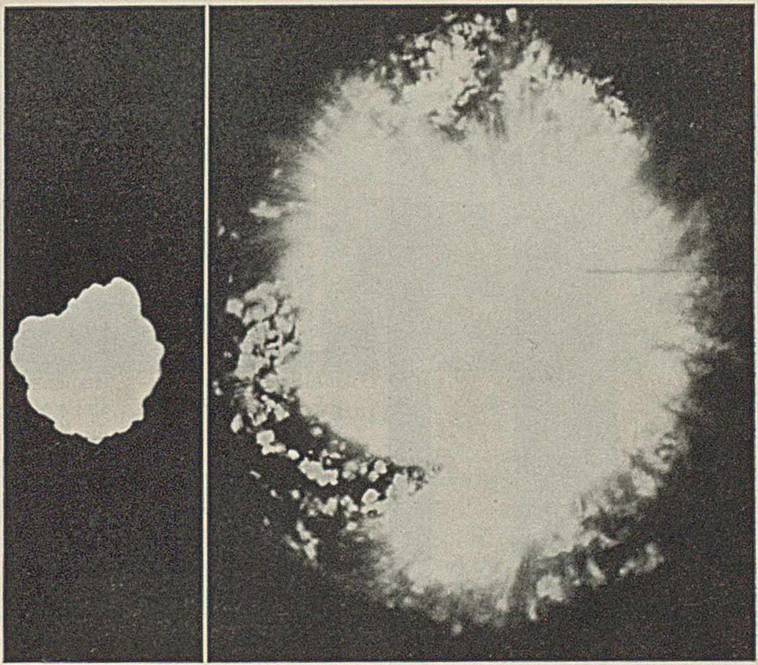


FIGURE 3. SINGLE PARTICLE OF KOLOFOG (× 60) BEFORE (AT LEFT) AND AFTER (AT RIGHT) FORMATION OF GEL BY ABSORPTION OF WATER

SELECTION OF PRODUCT FOR COMMERCIAL DEVELOPMENT

The selection of colloidal bentonite-sulfur for commercial development from several suggested products was not incidental to the utilization of waste material or by-products. The gelatinous colloidal properties of the new product first attracted attention. Early in the investigation it was recognized that bentonite-sulfur, when dispersed in water, resembles closely the gelatinous colloidal properties of Bordeaux "membranes," known to possess in a high degree the requisite adhesiveness and wettability. Thus, for the first time a sulfur fungicide had been produced possessing these highly desirable gelatinous or "membranous" properties of the best known copper fungicide. At the same time it was realized that possibly the new product could also be prepared in a substantially dry dispersible form for convenient use as a spray without any home-mixing operations in the orchard or field by the user, as must be done in the case of certain other standard fungicides, such as Bordeaux mixture. This same fact also appeared important in connection with the storage and shipment of the material and also gave it an important advantage in these respects over lime sulfur solution which must be shipped and used in liquid form, representing considerable inconvenience both to the shipper and user. Incidentally, attempts to produce a so-called dry lime sulfur had not proved satisfactory.

An additional advantage was the fact that the raw materials required for the production of the new fungicide—namely, elementary sulfur and bentonite—were commercially available in sufficient quantities to supply the entire requirements for a product designed for the uses mentioned, which annually require many thousands of tons of standard sulfur material in this country alone. The raw materials were also considered to be reasonably inexpensive.

METHOD OF MANUFACTURE

The raw materials employed are Wyoming bentonite or Wilkinite and ground mineral sulfur. A good grade of 99.9 per cent Texas sulfur is used. Wyoming bentonite is preferred because of its pronounced gelatinous colloidal properties and the very high percentage of suspensoids which are practically permanently suspensible in water. The bentonite is tested before use by a standard quantitative laboratory method of determining the suspensibility of the bentonite-sulfur which it produces. This test reproduces the actual manufacturing conditions closely and thus a uniform product is assured. Similar control tests are made regularly on samples from the regular factory runs.

Canadian bentonite, while apparently of good quality, occurs in deposits of thin strata and has, so far, not been conveniently obtainable in the market. Bentonite from California, Texas, and the eastern states has not proved entirely suitable.

The manufacture of Kolobase is conducted as follows: The bentonite is received loose in box cars, in pieces about the size of peas, and contains approximately 10 per cent moisture. It is ground in a Raymond four-roller mill until approximately 60 per cent will pass a 200-mesh screen and less than 1 per cent will remain on a 60-mesh screen. The sulfur is ground until 80 per cent will pass a 200-mesh screen and less than 0.5 per cent will remain on a 60-mesh screen. The equipment used in manufacture is shown diagrammatically in Figure 1. Four hundred pounds of the ground bentonite and two hundred pounds of the ground sulfur are thoroughly mixed in a flour blender, *A*, and elevated by means of the bucket elevator, *B*, to the hopper, *C*, which delivers the mixture to a feeding device, *D*. The latter passes the mixture to the first of four steam-jacketed insulated screw conveyors, arranged one above the other, *E*. The conveyors are heated by steam under 90 pounds pressure, and the steam line is equipped with a pressure gage and flowmeter (not shown). Each alternate conveyor is equipped with a recording thermometer, and all are provided with gas vents (not shown). The screws in the four conveyors are alternately right- and left-hand so that the material is passed back and forth through the set of four, while the screws may all be rotated in the same direction by chain drives from the speed reducer, *N*.

As the mixture of bentonite and sulfur progresses through the conveyors, moisture and sulfur dioxide are evolved, so that, when it emerges from the last conveyor, it contains only about 0.5 per cent moisture and is slightly acidic to methyl red indicator, whereas the bentonite is slightly alkaline to phenolphthalein before being processed. Also, the sulfur is now thoroughly absorbed into the bentonite so that the mixture is granular in character.

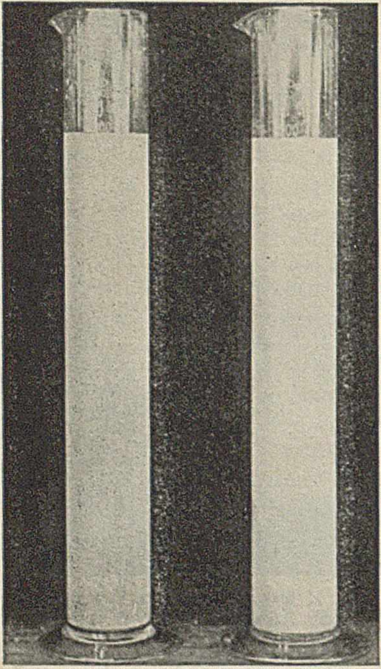


FIGURE 4. SIXTEEN-HOUR SUSPENSIONS OF BENTONITE (LEFT) AND KOLOFOG (RIGHT)

The hot reaction product is delivered from the lowest screw conveyor upon a slow-speed belt conveyor, *F*, which delivers it to a second bucket elevator, B^1, and also allows time for the temperature to drop well below the melting point of sulfur. The materials next pass through a hopper, *G*, to a slow-speed rigid-hammer pulverizer, *H*, the grids in which are spaced $^1/_8$ inch apart. After leaving the pulverizer, the product passes to a vibrating screen, *J*, equipped with a 24-mesh steel cloth. The fines collected in the hopper, *K*, are the product Kolofog. The oversize passes by means of the conduit, *M*, back to the bucket elevator, B^1, and again to the pulverizer.

The granular product Kolofog is for use in liquid sprays. If a product suitable for use as a dust is desired, the material is removed from the hopper, *G*, by means of a conduit, not shown, and is ground in a Raymond mill to a fineness of not less than 95 per cent through a 300-mesh screen.

COLLOIDAL PROPERTIES AND PARTICLE SIZE

The highly colloidal properties of bentonite-sulfur are at once apparent from the close resemblance of the finished product to the bentonite itself, both with respect to its highly gelatinous character as well as to the particle size of its permanent suspensions in water, under high magnification.

The gelatinous or hydrophylic properties are illustrated by the photographs shown in Figure 2, which show powdered bentonite and powdered bentonite-sulfur, respectively, in each of the upright beakers. The corresponding gels obtained by the slow absorption of approximately six parts by weight of water are shown in the inverted beakers. Except for the yellowish color of the bentonite-sulfur jelly, its general physical properties are hardly distinguishable from those of the bentonite jelly. The gel structure is further exhibited when the beakers are tapped with the fingers or rapidly shaken by any mechanical means which causes the gel to vibrate rapidly.

A further illustration of the highly hydrophylic or gelatinous character of the new product is given in Figure 3 which illustrates the appearance of a small single particle of bentonite-sulfur (Kolofog) on a microscope slide, under a magnification of about 102 diameters, before and after absorbing a limited amount of water "floated" over the particle. The tendency of the gel to break up into more minute gelatinous particles around the edges of the mass is also clearly shown. With still more water (as in the case of the 16-hour suspensions, shown in Figure 4) most of the smaller masses of the jelly become completely dispersed, forming a practically continuous phase between the relatively few particles of suspensoids and also between the masses of the thicker portions of the jelly. The presence of this substantially continuous phase of thin jelly is disclosed under "dark-field" illumination, which shows an enormous number of points of light exhibiting rapid Brownian movement (difficult to show photographically) corresponding to the ultramicroscopic particles of the bentonite-sulfur jelly between the larger masses and particles. Occasionally, with somewhat thicker suspensions or emulsoid solutions, the edges of this continuous phase or relatively thin jelly are discernible under the microscope at lower magnifications with ordinary illumination.

Exactly similar results to those described in connection with Figure 3 are obtainable with small particles of pure bentonite. This is true with respect to the appearance of the more dilute suspensions under the microscope, both with ordinary illumination and with so-called "dark-field" illumination. In fact, every microscopic procedure so far tried discloses no really definite characteristic differences as between the particles or masses of bentonite-sulfur (jelly) and those of bentonite itself. On the other hand, characteristic differences are clearly discernible in mere mechanical mixtures of bentonite and finely ground sulfur, although permanent (16-hour) suspensions cannot be prepared with such mixtures.

Figure 4 illustrates the rather close similarity in the appearance of suspensions of these two materials (bentonite and Kolofog) obtained after 16 hours of standing, using 1 gram of powdered material to 500 cc. of distilled water. Furthermore, the proportion of total solids remaining in suspension under these conditions is only slightly greater for bentonite than for Kolofog when pure materials are used. It will be observed, however, that the Kolofog suspension is somewhat more milky in appearance, probably owing to the thicker or slightly more gelatinous character of the semifluid emulsoid masses rather than to any appreciable difference in the size of the ultimate particles, as will be explained more fully later.

Perhaps the most significant fact, as already indicated, in connection with the colloidal properties of bentonite-sulfur, is the lack of any certain difference in the particle size or appearance of its permanent (16-hour) suspensions (prepared as above) and those of the bentonite itself, which is recognized as a highly colloidal material, as observed under the

TABLE I. COMPARISON OF TOXICITY OF BENTONITE-SULFUR AND OF SULFUR TO CONIDIA OF *Sclerotinia fructicola* (Americana)

SULFUR PREPARATION	EXPT. 1 (2-16-32)		EXPT. 2 (2-19-32)		EXPT. 3 (2-25-32)		EXPT. 4 (3-11-32)	
	Germ	Germ tube length	Germ	Germ tube length	Germ	Germ tube length	Germ	Germ tube length
	%	*Microns*	%	*Microns*	%	*Microns*	%	*Microns*
Bentonite-sulfur containing ground 300-mesh sulfur fused in bentonite, using 10% sulfur (dust)	3.7	10	0.2	...	0.2	10	0	...
Same, 5% sulfur (dust)	4.1	10	6.1	10	0.1	10	0	...
Same, 1% sulfur (dust)	5.4	10	2.3	15	0.5	10	1.4	10
Same, $^1/_3$% sulfur (dust)	10.9	10	10.2	15	4.0	15	26.6	20
Standard ground 300-mesh sulfur (dust)	58.1	90	77.8	150	23.9	90	52.3	90
Control	97.1	400	97.1	400	98.0	400	97.4	400
No. of spores counted for each test	1100		850		750		850	

A B C

FIGURE 5. PHOTOMICROGRAPHS (× 102) OF SUSPENSIONS

A. Bentonite suspension (16 hours)
B. Kolofog suspension (16 hours); ratio bentonite to sulfur, approximately 77:23
C. Temporary suspension of commercial wettable sulfur; ratio bentonite to sulfur, approximately 77:23

microscope even under very high magnification. In fact, it is extremely difficult to distinguish between the suspensions of the two materials in this way even when the suspensions are prepared in such manner as to contain the same proportion of bentonite to water. This is illustrated in Figure 5, which shows photomicrographs of permanent (16-hour) suspensions of bentonite (*A*) and Kolofog (*B*) prepared as described above and carefully concentrated to a slight extent so as to contain the same proportion of bentonite to water, the sulfur in the Kolofog suspensions representing an excess of suspended solid amounting to approximately 30 per cent of the weight of the bentonite present. The appearance, under the same conditions, of approximately the same percentage (30) of a well-known brand of commercial wettable sulfur temporarily suspended in the same amount of permanently suspended bentonite is shown in Figure 5*C*. It seems reasonable to conclude from this quantitative comparison that a considerable proportion, at least, of the suspended sulfur particles in Kolofog are really submicroscopic in dimensions under this magnification of 102.

The main significance of the preceding comparisons is that this new material possesses colloidal properties similar to those of the highest grade of bentonite, which, as previously stated, is generally recognized as a highly colloidal substance.

RELATION OF COLLOIDAL PROPERTIES TO TOXICITY, SAFETY, ADHESIVENESS, ETC.

The extremely high toxicity of fused bentonite-sulfur in comparison with that of a mechanical mixture of pure 300-mesh ground sulfur and ground bentonite, or with merely wettable sulfur generally is best explained on the basis, of the submicroscopic character of a considerable proportion at least, of the sulfur present in the bentonite-sulfur and to its highly colloidal character generally, although other explanations have been suggested.

Numerous direct determinations, by the spore count method, of the relative toxicity of bentonite-sulfur (Kolofog) in comparison with ground 300-mesh sulfur and typical ground wettable sulfurs have been made. These tests were conducted in accordance with the technic worked out by McCallan (*5*) and Wilcoxon and McCallan (*7*). Such tests have uniformly shown that spore germination is prevented or reduced to a substantial minimum, with radically lower concentrations of sulfur in the form of bentonite-sulfur than in any other form. Control tests on the toxicity of bentonite itself were always carried out in connection with these tests. Tables I and II give typical results obtained by this method.

The dusts were placed on 1 × 3 inch (2.5 × 7.6 cc.) glass slides by means of test tube dusters. Drops of a spore suspension were then placed upon the slides which were put in inverted moist chambers and sealed with water. After a period of hours, generally around 24, the germination counts were made under the low power of a microscope. The method has been described in detail by McCallan (*5*).

With low concentration of sulfur, particularly around 1 to 5 per cent, the toxicity, as determined by this method, of the sulfur in the form of bentonite-sulfur is of an entirely different order of magnitude from that of 300-mesh ground "wettable" sulfur when calculated upon the basis of the proportion of sulfur present. Also, substantially greater toxicity is obtained by this method with bentonite-sulfur containing $^1/_3$ per cent of sulfur than is obtained with 100 per cent of standard 300-mesh ground sulfur, both being used as dusts and then moistened with water (Table I).

In connection with toxicity tests of bentonite-sulfur dusts (Kolodust, etc.), Wilcoxon and McCallan (*7*) state: "Apparently, Kolodust retains its effectiveness after the rain test better than the other modified dusts. A possible explanation for this lies in the fact that the modification has actually produced a change in the physical state of the sulfur, and therefore it has qualities superior to that of sulfur dusts modified merely by mechanical additions." This statement is unusually significant in view of the extensive investigations carried on by these workers over a period of years on the toxicity of sulfur fungicides generally.

TABLE II. TOXICITY OF FUSED BENTONITE-SULFUR MECHANICALLY MIXED IN BENTONITE AND OF GROUND SULFUR MECHANICALLY MIXED IN BENTONITE

Dust	Expt. 3 (1-27-32)	
	Germ	Germ tube length
	%	*Microns*
5% bentonite-sulfur (containing $33^1/_3\%$ sulfur) equivalent to $1^2/_3\%$ sulfur in the form of bentonite-sulfur	14.5	...
$^1/_3\%$ bentonite-sulfur (containing $33^1/_3\%$ sulfur) equivalent to 0.111% sulfur in the form of bentonite-sulfur	50.9	...
Ground 300-mesh sulfur	53.5	...
5% 300-mesh ground sulfur (over 98% sulfur) equivalent to over 4.9% sulfur in the form of wettable sulfur	67.2	...
$^1/_3\%$ 300-mesh ground sulfur (over 98% sulfur) equivalent to over 0.32% sulfur in the form of wettable sulfur	81.4	...
Control	97.8	...
No. of spores counted for each test	900	

It follows from the foregoing that field data on the amount of sulfur remaining on the foliage and fruit after weathering, etc., must be interpreted in view of the toxicity or nature of the sulfur residue and not merely in terms of the total sulfur as has frequently been done. It has also been observed that the toxicity of bentonite-sulfur (Kolofog) is significantly increased by the addition of hydrated lime. This is contrary to the generally prevalent view that hydrated lime or a base producing an equivalent increase in the hydroxyl-ion concentration of sulfur suspensions produces a substantial decrease rather than an increase in toxicity.

Since Alexander (*1*) and Wherry (*6*) have shown that the ultimate particles of pure bentonite probably have a laminar structure with submicroscopic dimensions and also that a limited proportion are just visible microscopically in two dimensions (length and breadth) but submicroscopic in thickness, it seems plausible that the submicroscopic proportion of the sulfur in bentonite-sulfur, previously mentioned, is absorbed or adsorbed on or between the flat surfaces of these minute laminar particles of bentonite. This seems more probable in view of the fact that Wherry (*6*) has suggested that the water-adsorptive or gel-forming properties of bentonite are due to a similar absorption or adsorption of water between the layers or leaflets of these minute bentonite particles. Since the gel-forming properties of bentonite are not appreciably affected by the adsorption of fluid sulfur, it further appears probable that in the gel formed from bentonite-sulfur the adsorbed water is superimposed over the layer of adsorbed sulfur.

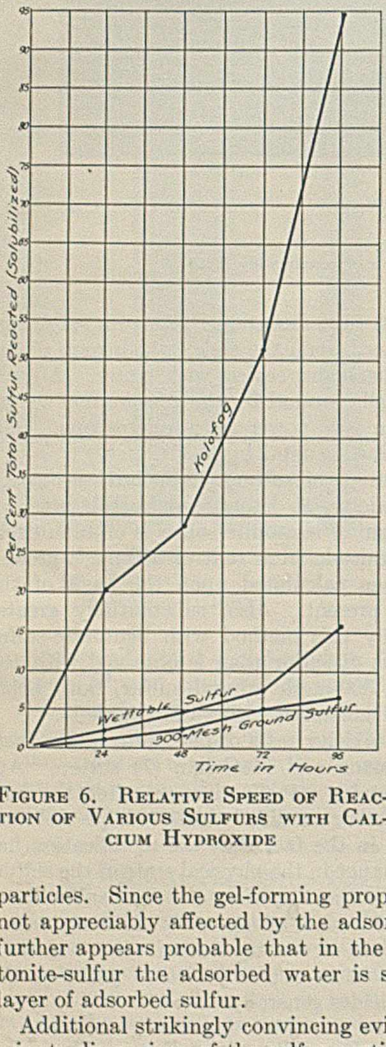


FIGURE 6. RELATIVE SPEED OF REACTION OF VARIOUS SULFURS WITH CALCIUM HYDROXIDE

Additional strikingly convincing evidence of the extremely minute dimensions of the sulfur particles in bentonite-sulfur is furnished by a determination of the rate or speed of chemical reaction between the sulfur in this form and solutions or suspensions of calcium hydroxide as compared with that of other forms of commercially available wettable or suspensible sulfur. In Table III is shown the amounts of materials which were placed in suspension and the amount of soluble reaction product calculated as sulfur. These results are shown graphically in Figure 6.

In carrying out this comparison of the relative speeds of reaction of bentonite-sulfur and wettable sulfur, the reaction mixtures were placed in 100-cc. stoppered cylinders, in 100 cc. of water and maintained at 96° F. (35.6° C.) in a thermostat, with equal stirring, in order to speed up the reaction so as to complete it in a reasonable time. The reaction progressed with unexpected swiftness. The transformation of sulfur into polysulfide was striking, and it was easy to tell the relative velocity of reactions by the depth of yellow color in solution. No attempt was made to determine polysulfide as such, owing to the fact that, in filtering the mixtures, considerable oxidation inevitably took place. Instead of determining the polysulfide, the total sulfur in solution was determined, which would include not only polysulfide but thiosulfate, sulfites, and sulfates. A blank run on the Kolofog and on the sample of wettable sulfur showed no sulfur in solution in the case of Kolofog and a negligible trace in the case of the wettable sulfur. The wettable sulfur employed is stated by its manufacturer to have a sulfur particle size ranging between 1 and 5 microns with an average of 3 microns.

Since the speed of a chemical reaction between a solid in suspension and a reacting substance in solution is known to be proportional in general to the surface of the solid (other factors being the same), it follows that the relative speeds under these circumstances are an indirect measure of the relative particle size of the different suspensions.

The radical difference in the speeds shown by the above data seems conclusive evidence that the sulfur particles in bentonite-sulfur are radically smaller than those of any known commercially obtainable wettable sulfur; this applies to the temporarily suspensible portion of the bentonite-sulfur as well as to the permanently (16-hour) suspensible portions of the new product.

These data also demonstrate that electrolytes, which are known to decrease the suspensibility of bentonite-sulfur, do not have any pronounced effect upon the particle size of the sulfur itself; otherwise the speed of the reaction would rapidly fall off, as it progresses, which is not the case.

TABLE III. COMPARATIVE SPEEDS OF REACTION OF BENTONITE-SULFUR AND WETTABLE SULFUR

REACTION MIXTURE	TOTAL SULFUR REACTED 24 hours %	48 hours %	72 hours %	96 hours %
Kolofog, 3.07 g. (= 1 g. sulfur); hydrated lime, 1 g.	20.12	28.98	51.83	94.42
Wettable sulfur, 1.29 g. (= 1 g. sulfur); hydrated lime 1 g.	2.42	4.47	7.79	15.7
300-mesh sulfur, 1 g.; hydrated lime, 1 g.	1.158	2.29	3.96	6.63
Blank on 3.07 g. Kolofog	0.00	0.00	0.00	0.00
Blank on 1.29 g. wettable sulfur	0.005	0.005	0.005	0.005

With respect to the safety of bentonite-sulfur, the fact that the sulfur is present in elementary form rather than in that of soluble sulfur compounds, as is the case with lime sulfur solution, for example, insures a wide margin of safety of the material to the foliage or growing plant. Thus, this new product represents really important progress toward the solution of the fundamental problem outlined at the beginning of this paper—namely, the provision of a sulfur fungicide of extremely high toxicity, which, at the same time, possesses a wide margin of safety.

On the other hand, the highly gelatinous and sticky character of bentonite-sulfur accounts for its adhesiveness, wettability, and spreadability; the jelly becomes more fluid as more water is absorbed and finally, with the addition of still more water, as in the case of the spray tank suspension, forms a liquid dispersion of the extremely minute masses of the jelly with a substantially continuous phase of very thin jelly between these particles, as explained above. Upon drying down, the colloidal bentonite-sulfur tends to become irreversible or, perhaps more accurately speaking, partially coagulates, especially on the surface, forming a relatively insoluble coating over the foliage or the surface of the plant to which it has been applied. In this respect the new product differs radially in an important respect from the ordinary "stickers" and wetting agents which have previously been proposed for this purpose. Thus, the new product combines to a high degree the essentially inconsistent or opposed properties of adhesiveness or weather-resisting properties and wettability as already emphasized above.

Electrolytes, except weak electrolytes or very dilute solutions, tend to break up the gelatinous structure of bentonite-sulfur jellies. In this manner the adhesiveness of the material may be controlled, an important point in connection with the removal of arsenical residues where this is desired or necessary. Hydrated lime (added to the spray mixture) permits removal of the residue without decreasing the adhesiveness in any objectionable degree.

FIELD DATA ON FUNGOUS DISEASE CONTROL

While it is believed that the final test of the control value of a fungicide is to be found in the actual commercial results obtained and the satisfaction which the material gives in the hands of the grower himself, nevertheless actual data on the percentage of total scab on the fruit, with and without the use of the fungicide, the percentage of scab infection on the foliage during the growing season, etc., is of considerable significance in this connection. Illustrative field data given by Boyd (*3*) are as follows:

FUNGICIDE	APPLES SPOTTED BY SCAB	
	McIntosh	Baldwin
	%	%
Liquid lime sulfur	17.3	3.7
Kolofog spray	11.2	3.1
Check	83.3	50.4

As illustrative of the almost perfect control of apple scab that may be secured with Kolofog when timely applications are made, the following data obtained by Dye (*4*) are presented:

TREATMENT	SCAB
	%
Check	95.7
Kolofog, 3 lb. in 50 gal.	1.6
Kolofog, 4 lb. in 50 gal.	1.5

ACKNOWLEDGMENT

Acknowledgment is made to Max L. Tower, H. W. Dye, and J. F. Les Veaux, of the Niagara Sprayer and Chemical Company, Inc., and to H. H. Whetzel, L. M. Massey, and R. A. Hyre, of Cornell University, for valuable data and suggestions in connection with the preparation of this paper.

LITERATURE CITED

(1) Alexander, Jerome, *Colloid Symposium Monograph*, **11**, 99-105 (1924).
(2) Banks, H. W., U. S. Patent, 1,550,650 (Aug. 18, 1925); McDaniel, A. S., *Ibid.*, 1,934,989 (Nov. 14, 1933).
(3) Boyd, O. C., *Mass. Fruit Growers Assoc., Rept. 38th Ann. Meeting*, 1932.
(4) Dye, H. W., unpublished data.
(5) McCallan, S. E. A., Cornell Univ. Agr. Expt. Sta., *Mem.* **128**, 10-12 (1930).
(6) Wherry, E. T., private communication (quoted by Alexander, *1*), *J. Wash. Acad. Sci.*, **7**, 576-83 (1917).
(7) Wilcoxon, Frank, and McCallan, S. E. A., *Contrib. Boyce Thompson Inst.*, **3**, 513-14 (1931).

RECEIVED January 18, 1934. Through the financial assistance of the Niagara Sprayer and Chemical Company, Inc., this paper has been printed earlier than would otherwise have been possible.

Rubber Plasticity Control

Significance and Value of Recovery Measurement of Williams Plastometer

J. H. DILLON, Firestone Tire and Rubber Company, Akron, Ohio

Experiments to determine the practical value of the recovery measurement of the Williams plastometer in rubber plasticity control testing are described. An empirical relation between y value and time of milling was found for gum rubber on a cold laboratory mill. This relation furnishes a convenient method of analysis of the Williams plastometer indices. The relation between these indices was investigated with respect to amount and method of breakdown of the rubber and to the degree of set-up of typical factory stocks. No marked advantage of the recovery measurement over the usual y value measurement, from a practical standpoint, was discovered for the samples of crude rubber and rubber stocks tested. Some results obtained with an extrusion plastometer operating at high rates of shear are given which indicate that the extrusion type of plastometer offers a better criterion of plasticity of rubber than does the compression instrument.

THE original compression plasticity test for rubber, as developed by Williams (*14*), consisted in measuring the compressed height (y value) of a 2-cc. rubber sample after a standard time of compression under a 5-kg. load at a standard temperature. No account was taken of the increase in height—i. e., recovery, of the pellet after removal of the load. The distinction between plastic flow and pseudoplastic flow in the compression test, as applied to rubber, was first made by van Rossem and van der Meijden (*10*). They measured deformation of masticated rubber under load as a function of time of compression, and then removed the load and measured the recovery as a function of time. They showed that the ratio of the plasticity to the elasticity in the masticated rubber is a rapid function of temperature, increasing from zero at 16° C. to a very large value at 70°. Karrer (*6*) adopted the viewpoint of van Rossem and van der Meijden and suggested a definition of plasticity which included the total deformation of a pellet of standard dimensions under a standard compressive force acting for one second and its recovery after removal of the load. This definition, when given quantitative form, applied only to one type of measuring instrument, the Goodrich plastometer. Hence, the definition was purely arbitrary and was justified only in that it took account of one more variable than does the Williams y value.

Karrer designed a plastometer (*7*) which was also adapted to the measurement of recovery, and in which the compressive force acted for a definite short-time interval. The plastometer platens were of the same type as those used by van Rossem and van der Meijden; that is, the platen faces were of the same area (one sq. cm.) as the ends of the cylindrical pellet. A simpler plastometer (*8*) which differed only in that it operated under a dead load was designed for control work.

The arguments of the various investigators (*6, 10, 12*) in regard to the significance of recovery in plasticity measurements have been of definite value in clarifying what had been a somewhat vague conception of plasticity among rubber technologists. Certainly the basic idea, as maintained by Karrer, van Rossem, and van der Meijden, that the

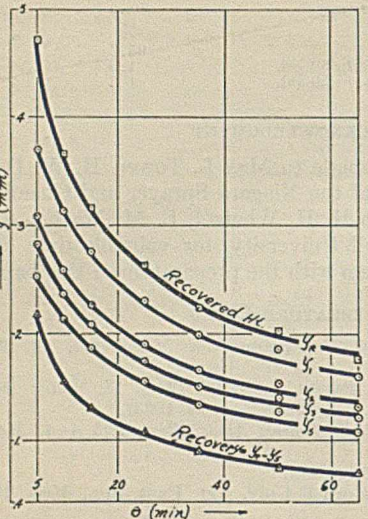


FIGURE 1. WILLIAMS PLASTOMETER INDICES AS FUNCTIONS OF TIME OF MILLING (θ)

Pale crepe; plastometer at 100° C.; cold 30.5 × 15.2 cm. mill

Williams plastometer y value is a measure of both the plastic mobility and the elastic modulus of the rubber is correct. However, the proponents of the recovery measurement have neglected one important factor—namely, the dependence of elastic recovery upon speed of deformation. It has been shown by Dillon and Johnston (*3*), in connection with experiments on an extrusion plastometer, that elastic recovery is a rapid function of the speed of deformation of the rubber (rate of shear). Furthermore, it has been shown mathematically (*3*) that, for the Williams plastometer, the rate of shear for a given testing time varies inversely as the $^3/_2$ power of y. It has been shown also (*3*) that, for the Goodrich plastometer, the mean rate of shear is given by

$$\frac{\overline{dv}}{dy} = \frac{9RK}{16}\, y \qquad (1)$$

where R = original radius of pellet
y = separation of plates at time t
$K = \frac{1}{t}\left(\frac{1}{y^2} - \frac{1}{y_0^2}\right)$
y_0 = original height of pellet

Hence
$$\frac{\overline{dv}}{dy} = \frac{9Ry}{16t}\left(\frac{1}{y^2} - \frac{1}{y_0^2}\right) \qquad (2)$$

For a given testing time, t, the mean rate of shear is a function of y for the Goodrich plastometer also. Thus the elastic recovery must be a rapid function of y value in both types of compression plastometer. It follows directly, then, that the recovery measurement is not only a measure of the residual elasticity of the rubber but also of the plastic properties. It is to be expected, therefore, for a given rubber stock at least, that the y value and recovery measurements should correlate. This conclusion is verified by the results of the present investigation.

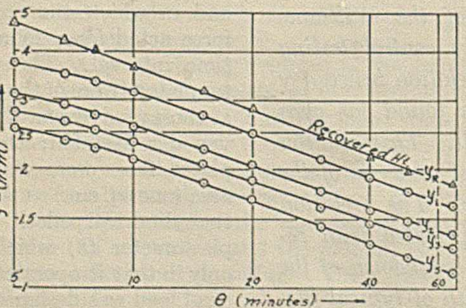


FIGURE 2. WILLIAMS PLASTOMETER INDICES AS FUNCTIONS OF MILLING TIME (θ), USING LOGARITHMIC COÖRDINATES

Pale crepe; plastometer at 100° C.; cold 30.5 × 15.2 cm. mill

It would seem, because of the importance which recovery assumes in an academic sense, that the measurement of recovery should have practical importance in plasticity control testing. However, the author has been unable to find in the literature (*1–15*) any data to show that the measurement of recovery on different batches of a given stock provides any information in addition to that yielded by the simple measurement of y value. Garvey (*4*) has presented some interesting results on the relation between the retentivity and softness, as measured by the Goodrich plastometer, as a function of degree of vulcanization. He plotted the softness against the retentivity for several testing temperatures. The resulting straight lines have different slopes, depending on the time of cure. These particular results are hardly applicable to plasticity control testing, although they suggest that the measurement of recovery at two or more temperatures may be very useful in this regard. He has also stated that the retentivity-softness relation is useful in differentiating tough, crude rubber from scorched rubber. Inasmuch as these latter results have not yet been published, they cannot be considered here. Karrer, Davies, and Dietrich (*8*) have given experimental data which show that recovery and y value, as measured by the Goodrich plastometer, are not simply related for different stocks. The data do show, however, that for crude rubber and gum stocks there is very good correlation between recovery and y value. Furthermore, the curves giving the relation between recovery and time of milling are similar to the curves giving y value (softness) as a function of time of milling. Since plasticity control consists mainly in comparing the plastic properties of different batches of a given stock, it was necessary to perform some simple experiments described in this paper in order to decide whether or not factory control information could be obtained from recovery measurements with a Williams plastometer which could not be gained through measurement of y value alone.

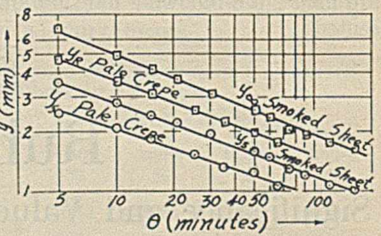


FIGURE 3. WILLIAMS PLASTOMETER INDICES AS FUNCTIONS OF MILLING TIME (θ)

Pale crepe and smoked sheet; plastometer at 100° C.; cold 30.5 × 15.2 cm. mill

EXPERIMENTAL PROCEDURE

Two somewhat different methods of measuring recovery were employed. The first consisted simply in obtaining the y value, removing the compressed pellet from the press exactly at the end of the 5-minute compression period, and measuring the recovered thickness of the pellet 24 hours later at room temperature, with an ordinary thickness gage. This recovered thickness was recorded as y_∞.

The second method, which is more accurate than the first, is as follows: The thickness gage was placed in the plastometer oven and allowed to come up to the testing temperature (85° C. for compounded stocks, 100° C. for crude rubber and master batches). The whole test was performed in the same oven at constant temperature. The 2-cc. cylindrical pellet (not preheated) was placed between the platens of the plastometer and compressed for 5 minutes. Readings of the plastometer gage giving the thickness of the pellet (= y) were taken at various intervals during the compression (usually after 1, 3, and 5 minutes of compression). Exactly at the end of the 5-minute compression period, the y_5 value was noted, and the load was removed from the pellet which was transferred quickly to the thickness gage (from which the loading weight and lifting handle had been removed) and allowed to recover for 5 minutes. The recovered thickness was then recorded as y_R.

The second method appears superior to the first in that certain errors introduced by uneven shrinkage of the pellets during cooling are eliminated. In practice, however, it was found that the results of the two methods correlated within the limits of experimental error.

Only the quantities y_5 and y_R or y_∞ were considered in this work. The recovery difference function, $(y_R - y_5)$ or $y_\infty - y_5)$, was not employed for the following reasons: It has been found that, when the recovery $(y_R - y_5)$ was of the same order of magnitude as y_R, $(y_R - y_5)$ varied in practically the same manner as y_R alone. When $(y_R - y_5)$ was much smaller than y_R, $(y_R - y_5)$ varied more rapidly than y_R, but the percentage error in $(y_R - y_5)$ was much larger than in y_R. This is to be expected, of course, for the same total error exists in $(y_R - y_5)$ as in y_R. Thus, for $y_R - y_5 \ll y_R$, the value of $(y_R - y_5$ is of the same order of magnitude as the probable error in y_R and calculation of the recovery has very little meaning.

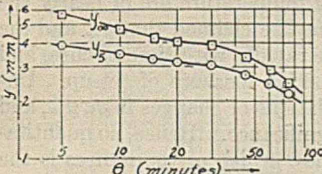


FIGURE 4. WILLIAMS PLASTOMETER INDICES AS FUNCTIONS OF MILLING TIME (θ)

Smoked sheet; plastometer at 100° C.; hot 30.5 × 15.2 cm. mill

EMPIRICAL RELATIONS BETWEEN WILLIAMS PLASTOMETER RESULTS AND TIME OF MILLING

The plastic state of a finished rubber stock is determined mainly by three factors: Initial plastic state of the crude rubber, nature and amount of mechanical treatment given the rubber, and amount of premature vulcanization (set-up) introduced during processing. In order to study the significance of the Williams plastometer indices (y value and recovery), it was necessary to determine the dependence of the indices upon these three fundamental factors.

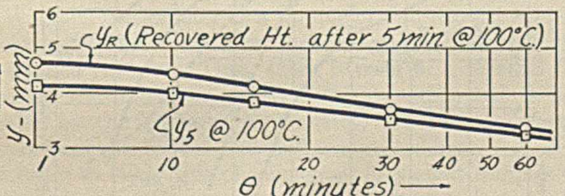


FIGURE 5. WILLIAMS PLASTOMETER INDICES AS FUNCTIONS OF MILLING TIME (θ)

Carbon-black master batch; plastometer at 100° C.; cold 30.5 × 15.2 cm. mill

The effect of mechanical treatment upon y value and recovery was studied by investigating their relations to time of milling. Samples of the crude rubber or rubber compound were placed on the rolls of a cold 12 × 6 inch (30.5 × 15.2 cm.) laboratory mill (ratio of roll speeds = 1.10) and were cut for 120 minutes or less. Samples were taken from the batches at intervals during the milling process, and measurements of y value (y_1, y_2, y_3, y_5) and recovered y value (y_R or y_∞) were made as described under Experimental Procedure. Two determinations were made on each sample. The average y values, recovered y value, and also the recovery $(y_R - y_5)$ for a 1000-gram batch of pale crepe are plotted as functions of milling time in Figure 1. The curves are of the familiar form and are all approximately parallel. These same data are plotted logarithmically in Figure 2; parallel straight lines result in the interval of milling times 8–65 minutes.

Figure 3 shows another logarithmic plot of these results for pale crepe, and also of those for a 1000-gram batch of smoked sheet. The curves are linear and have nearly the same slope.

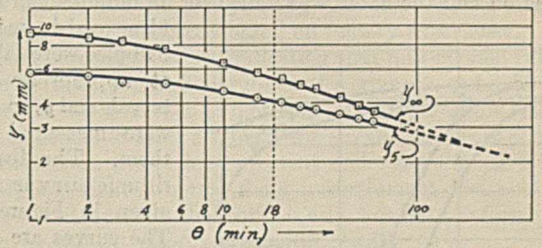


FIGURE 6. WILLIAMS PLASTOMETER INDICES AS FUNCTIONS OF MILLING TIME (θ)

Smoked sheet; plastometer at 100° C.; water-cooled 213.4 × 61 cm. mill

The linear form of these parallel logarithmic curves suggests the existence of an empirical equation of the form:

$$y_t = b_t\Theta^m \tag{3}$$

where y_t = y value or recovered y value (at testing time t) corresponding to a milling time, Θ
b_t = a constant characteristic of testing time t
m = a constant characteristic of these types of rubber on this particular cold mill

Equation 3 applies to rubber on a cold 12 × 6 inch (30.5 × 15.2 cm.) mill. The slope of the curves gives the value of m as -0.364.

The form of these logarithmic curves may be interpreted to mean, for this particular case, that both y_5 and y_R obey the same law expressed by Equation 3—i. e., are the same functions of the parameter, Θ. Thus, for detection of plasticity variations in massed crude rubber due to different amounts of breakdown under these particular conditions, measurements of y value and recovery tell the same story. In other words, in so far as it is desired to detect varying amounts of a given type of mastication of gum rubber, measurement of recovery appears to be a superfluous operation.

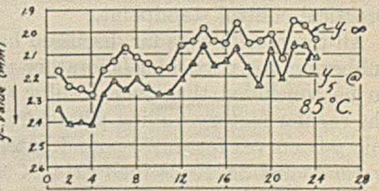


FIGURE 7. DIRECT CORRELATION BETWEEN y VALUE AND RECOVERY

Twenty-six factory batches of a tube stock; Williams plastometer at 85° C.

A similar logarithmic plot for smoked sheet on a hot 12 × 6 inch (30.5 × 15.2 cm.) laboratory mill is shown in Figure 4. The data were obtained as follows: A batch of smoked sheets was cut on the laboratory mill with no cooling water in the rolls and the y_5 and y_∞ values were measured on samples taken from the batch at various intervals during the milling. The curves are approximately linear, though not quite parallel in the interval of milling times 5–30 minutes. At Θ = 30 minutes, the slopes of the curves change greatly, and they are no longer linear. However, the curves are similar and it seems that, for this case also, no information in addition to that furnished by measurement of y_5 is gained by measuring y_∞. It is true that the curves indicate that y_∞ gives a slightly more sensitive measure of amount of mastication than does

y_5. This advantage is nullified, however, by the larger chance of error in y_∞ or y_R, whichever is measured.

In order to determine whether a highly pigmented rubber stock behaves in the same manner on the mill as does pure gum, a carbon-black master batch (28 volumes of carbon black, 100 volumes of rubber) was milled as follows: A 1200-gram sample of the master batch was placed on the hot laboratory mill and cut for 5 minutes. The cooling water was then turned on and the batch was milled for 55 minutes more on the cold mill. Samples were taken at appropriate intervals and y_5 and y_R were measured on them. The logarithmic curves are given in Figure 5. The curves are approximately linear but not parallel. It is possible in this case, therefore, that recovery is a slightly more sensitive measure of degree of breakdown than is y value alone; i. e., the quantity, m, is larger for the $(y_R - \Theta)$ curve than for the $(y_5 - \Theta)$ curve. Except for this slight advantage in sensitivity, however, y_R and y_5 obey the same type of power law in Θ. Hence they cannot be said to measure greatly differing properties, and it is doubtful whether the measurement of both y value and recovery is justified from a practical control standpoint.

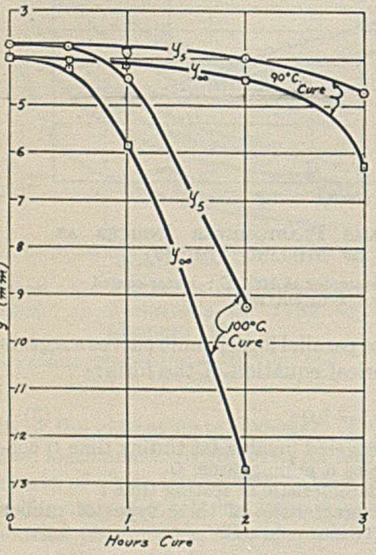


FIGURE 8. WILLIAMS PLASTOMETER INDICES AS FUNCTIONS OF TIME OF CURE

Tread stock (26 per cent carbon black by volume on the rubber, accelerated by mercaptobenzothiazole); plastometer at 100° C.

All the results thus far discussed have been obtained from rubber on one particular laboratory mill. By no means is it to be concluded that such results will apply accurately to the regular factory milling procedure. In fact, the logarithmic y-Θ curves for a 300-pound batch of smoked sheet on a water-cooled 84 × 24 inch (214 × 61 cm.) mill (front roll speed = 115 feet per minute, back roll speed = 124 feet per minute) were somewhat different from those for the cold laboratory mill (Figure 6). Here the curves were neither linear nor parallel. In fact, they appeared to be approaching each other, as shown by the extrapolated dotted lines; i. e., the rubber was approaching the true dead-milled state where the recovery becomes negligibly small. The rubber is usually batched off at Θ = 18 minutes. Thus, from a practical standpoint no great advantage of the recovered y_∞ measurement over the y_5 measurement appears in this case, for the curves are of similar form in the interval 0–18 minutes.

DIRECT CORRELATION BETWEEN y VALUE AND RECOVERED y VALUE FOR COMPOUNDED STOCKS

A number of correlations have been made on factory batches of regular compounded stocks. For example, in Figure 7 are shown the y_5 and y_∞ data for twenty-four batches of a tube stock accelerated by an aldehyde amine type of accelerator. No significant departures from good correlation appear. Thus, no practical advantage to be gained from the y_∞ measurement is apparent from this type of investigation.

WILLIAMS PLASTOMETER RESULTS IN RELATION TO SET-UP

Premature vulcanization (set-up) of rubber stocks, resulting from abnormally high milling temperature, too high tubing speeds, improper compounding, or storage in large rolls, is another important factor to which the results of a plasticity control instrument must be sensitive. In order to compare the y value and recovered y value measurements with respect to the degree of set-up, samples of typical tread and tube stocks were heated at 90° and 100° C., for times varying from 0 to 3.5 hours, and plasticity measurements were made on them. Figure 8 shows the indices y_5 and y_∞ plotted as functions of time of cure for a tread stock (26 per cent carbon black by volume; accelerator, mercaptobenzothiazole). The curves for a given curing temperature are of nearly the same form. Here again it may be claimed that y_∞ and the recovery $(y_\infty - y_5)$ vary more rapidly with time of cure, and furnish therefore a more sensitive measure of set-up. Unfortunately, percentage calculations of changes in y_5, y_∞, and $(y_\infty - y_5)$ have very little significance. Hence, no quantitative proof can be given to show which of the indices is the most sensitive in respect to any variable. It should be remembered, however, that the recovery measurement is subject to the inaccuracies inherent in any quantity, which is the small difference between two large quantities. Furthermore, in measuring y_∞ or y_R, an additional measuring operation is required, and hence y_∞ or y_R is subject to more error than is y_5. This reasoning is fully borne out by experience.

A similar set of curves for a typical tube stock accelerated by an aldehyde amine is shown in Figure 9. The same remarks made in connection with the curves of Figure 8 apply also here.

Another curve is plotted in Figure 9, obtained with the same samples (90° C. cure) with an extrusion plastometer described elsewhere (3). The efflux rate (volume extruded in unit time at a constant driving pressure and temperature, as measured in the extrusion plastometer, varies much more rapidly with time of cure than do the Williams plastometer indices.

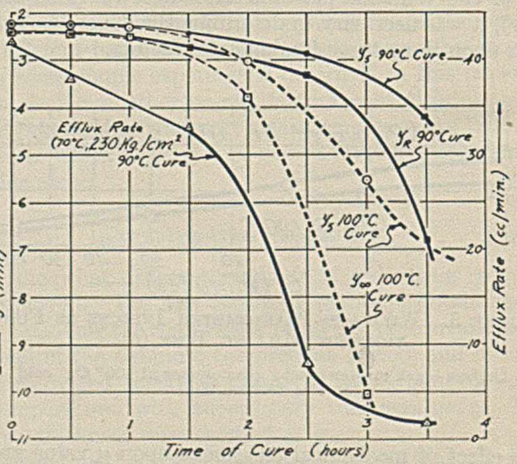


FIGURE 9. WILLIAMS AND EXTRUSION PLASTOMETER INDICES AS FUNCTIONS OF TIME OF CURE

Tube stock accelerated by an aldehyde amine; Williams plastometer at 100° C.; extrusion plastometer pressure = 3270 pounds per square inch (229.9 kg. per sq. cm.) at 70° C.

Excluding the results of the extrusion plastometer from the discussion, these data fail to show that the recovery measurement of the Williams plastometer is superior to the usual y value measurement in detecting set-up in these typical stocks.

PLASTICITY MEASUREMENTS ON PLASTICATED AND MILL-MASSED RUBBER

Two distinctly different types of masticating machines are employed in modern rubber plants, mills, and plasticators. The experience in this plant has been that rubber, plasticated in the Gordon machine, which gives the same y_5 value with the Williams plastometer as a sample of mill-massed rubber, appears much stiffer in factory processing operations than the mill-massed rubber. Thus, there is need of a method for detecting the difference, which certainly exists but is not revealed by the Williams plastometer, between the plastic properties of plasticated and mill-massed rubber.

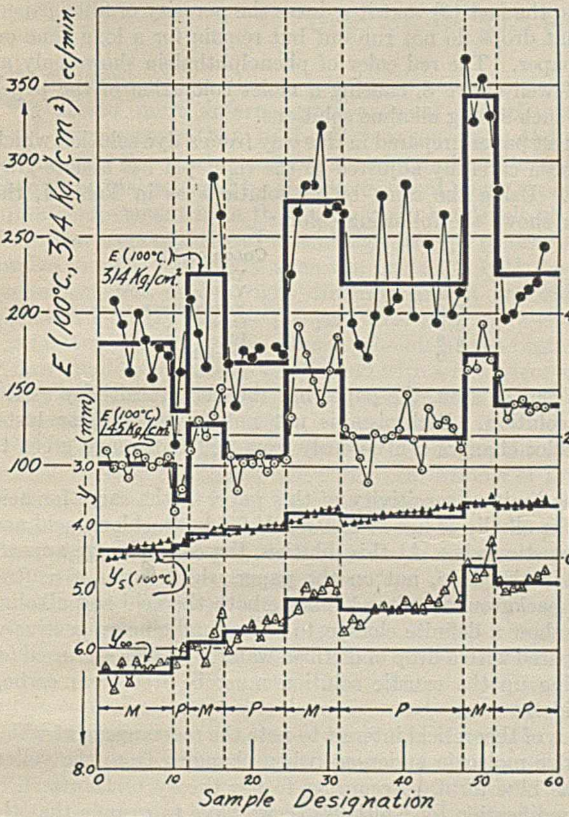


FIGURE 10. WILLIAMS AND EXTRUSION PLASTOMETER INDICES AS MEASURED ON FIFTY-EIGHT BATCHES OF PLASTICATED AND MILL-MASSED SMOKED SHEET

Williams plastometer at 100° C.; E = efflux rate of extrusion plastometer; heavy horizontal lines give average data in each group.

In order to study this phenomenon, fifty-eight samples of plasticated and mill-massed smoked sheet were selected in a range of y value (3.5 to 4.5 mm.), and three types of plasticity tests were made on them. The Williams plastometer indices y_5 and y_∞ were measured as described under Experimental Procedure. Plasticity measurements at 100° C. were also made with the extrusion plastometer (*3*) with two driving pressures, 2060 and 4480 pounds per square inch (145 and 316 kg. per sq. cm.). The results are plotted in Figure 10 in the form of correlation curves. The data are separated into groups according to y_5 value and the type of the masticating process employed—i. e. plasticated (P) or mill-massed (M). The averages of the readings in the various groups are indicated by the heavy horizontal lines.

It is quite clear that the y_5 measurements do not correlate with the extrusion plastometer results. The latter are seen to be much more sensitive to variations in plasticity than are the Williams plastometer indices. The extrusion plastometer results indicate definitely that mill-massed rubber is softer than plasticated rubber yielding the same y_5 value, thus agreeing with conclusions based on factory experience. The y_∞ curve is contradictory, indicating that mill-massed rubber is softer than plasticated rubber of a given y_5 value in two cases and the reverse in two others. Hence, it seems reasonable to conclude that, although the y_∞ measurement is more sensitive than the y_5 measurement and agrees in part with factory experience whereas the y_5 measurement does not, still it does not furnish the consistently accurate information given by the extrusion plastometer results.

CONCLUSION

The experiments described in this paper were undertaken in an effort to discover under what conditions the recovery measurement has practical value in plasticity control testing. No conditions were found where the recovery measurement yielded any important practical information which could not be gained by measurement of y value alone. It must be borne in mind that no experiments of this nature can be considered as perfectly general. Certain cases, not specifically included in the experimental conditions employed, may exist where measurement of recovery has definite practical value. Furthermore, great caution should be exercised in applying these results to any types of compression plastometers other than the standard Williams instrument with which the tests were made.

ACKNOWLEDGMENT

In conclusion the author wishes to thank N. Johnston and O. D. Cole for their suggestions which helped materially in carrying out this work, and N. A. Shepard under whose direction this work was done.

LITERATURE CITED

(1) Dietrich, E. O., IND. ENG. CHEM., 21, 769 (1929).
(2) Dietrich and Davies, *Ibid.*, Anal. Ed., 3, 297 (1931).
(3) Dillon and Johnston, *Physics*, 4, 225 (1933).
(4) Garvey and White, IND. ENG. CHEM., 25, 1042 (1933); Garvey and Thompson, *Ibid.*, 25, 1292 (1933).
(5) Grenquist, E. A., *Ibid.*, 22, 759 (1930).
(6) Karrer, E., *Ibid.*, 21, 770 (1929).
(7) Karrer, E., *Ibid.*, Anal. Ed., 1, 158 (1929).
(8) Karrer, Davies, and Dietrich, *Ibid.*, 2, 96 (1930).
(9) Peek, R. L., *J. Rheol.*, 3, 345 (1932).
(10) Rossem, van, and Meijden, van der, *Rubber Chem. Tech.*, 1, 393 (1928).
(11) Scott, J. R., *Inst. Rubber Ind. Trans.*, 7, 169 (1931).
(12) Usherwood, G. W., *Ibid.*, 8, 227 (1932).
(13) Vries, O. de, *Arch. Rubbercultuur*, 9, 260 (1925).
(14) Williams, Ira, IND. ENG. CHEM., 16, 362 (1924).
(15) Winklemann and Croakman, *Ibid.*, 22, 865 (1930).

RECEIVED September 20, 1933. Presented before the Division of Rubber Chemistry at the 86th Meeting of the American Chemical Society, Chicago, Ill., September 10 to 15, 1933.

HEAT-STOPPER. One of the biggest barriers to development of air-conditioning may be removed by the new type of glass announced by Corning Glass Works. The new glass, christened Aklo, has the unusual property of transmitting 70 per cent of the visible energy in the sunlight which strikes it, but of holding back the heat rays so that barely 30 per cent of them pass through. Thus the Aklo window pane brings in the wanted light with a minimum of the summer heat. Energy in summer sunlight is distributed with roughly 44 per cent in the visible region, 4 per cent in the ultra-violet, and 52 per cent in the infra-red or heat rays. The air-conditioning bills, in the case of Aklo-glazed houses, will be lower because heat does not come through windows.

Nitrazine Yellow, a New Indicator

HENRY WENKER, 425 Cherry St., Elizabeth, N. J.

MANY indicators have been introduced for the purpose of refining the methods of pH determination. While these newer indicators fill an actual need, their individual usefulness is necessarily restricted to a limited pH range, which in many cases lies well below or above the neutral point of pH 7. Litmus solution and litmus paper, because of their favorable pH range, still are widely used for the titration of acids and alkali to neutral, and for rapid tests whether a solution has an acid, alkaline, or neutral reaction.

A new indicator which has certain advantages over litmus is 2,4-dinitrobenzene-azo-1-naphthol-3,6-disulfonic acid, a yellow dye for which the author suggests "nitrazine yellow" as a convenient name.

Nitrazine yellow forms red crystals which dissolve easily in water and in dilute acids and alkali. The acid solution has a bright yellow color; the alkaline solution is bright deep blue. The solution in distilled water has a red-brown color, due to partial conversion of the dye into its blue ionogen form. The dyestuff also dissolves readily in 80 per cent alcohol, but is almost insoluble in 96 per cent alcohol. The solution in concentrated sulfuric acid is bright blue.

The pH range of nitrazine yellow was determined by the use of buffer solutions made from 0.1 *M* primary potassium phosphate solution (13.620 grams per 1000 cc.) and 0.05 *M* borax solution (19.110 grams of $Na_2B_4O_7.10H_2O$ per 1000 cc.) according to Kolthoff (*1*). For 10 cc. of buffer solution, 0.2 cc. of 0.05 per cent dye solution was used (buret).

TABLE I. PH RANGE OF NITRAZINE YELLOW

PHOSPHATE SOLUTION Cc.	BORAX SOLUTION Cc.	PH	COLOR OF SOLUTION
8.77	1.23	6.0	Yellow
8.30	1.70	6.2	Yellow, slightly duller
7.78	2.22	6.4	Pale yellow
7.22	2.78	6.6	Pale gray
6.67	3.33	6.8	Pale blue
6.23	3.77	7.0	Blue

The pH range of nitrazine yellow, according to Table I, is 6.0 to 7.0, with a sharp neutral point at pH 6.6. However, the color change between pH 6.0 and 6.4 and between 6.8 and 7.0 on the other side is so small that for practical titration purposes almost the entire color change takes place between pH 6.4 and 6.8.

Dye solutions of the concentration given above show no dichroism; in more concentrated solutions, however, dichroism is pronounced, the color of the solution changing from yellow through purple and violet shades to blue, especially in thick layers.

In titration tests, 0.5 cc. of 0.1 per cent dye solution was used for 250 cc. of distilled water. Complete color change from bright yellow to bright blue and vice versa was caused by 0.3 cc. of 0.1 *N* caustic soda and 0.1 *N* hydrochloric acid, respectively. The same result was obtained in concentrated solutions of neutral salts, such as sodium chloride, sulfate, or nitrate.

Because of its sensitivity and sharp color contrast nitrazine yellow is naturally well suited for the preparation of a high-grade test paper. For the same reasons, the preparation of nitrazine paper is a difficult process, requiring considerable care and experience to obtain uniform high quality. During these experiments it has been found that by addition of a certain amount of phenolphthalein to the dye solution the sensitivity of the resulting paper can be greatly increased. This is due not to the indicator properties of phenolphthalein, but to the fact (*2*) that it reduces the porosity of filter paper, so that drops do not run out but remain for a long time on the paper. The red color of phenolphthalein shows only at a pH well above 8, causing a violet coloration of the paper with such strong alkaline solutions.

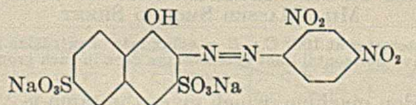
A test paper prepared in this way from a dye solution which has been carefully adjusted to the right pH has a slate-gray color. Using the same buffer solutions as in Table I, the paper shows the following colors:

PH	COLOR OF PAPER
6.0	Yellow
6.2	Yellow
6.4	Yellow-green
6.6	Green
6.8	Blue
7.0	Dark blue

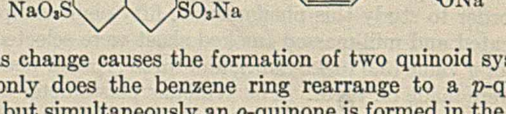
As can be seen, the paper has the same sensitivity as the dye solution. Dichroism is not noticeable in these tests; the color changes continuously from yellow through green to blue.

The limit of sensitivity of this paper is the same for acid and for alkali; it lies at 0.00001 *N* for hydrochloric acid and for caustic soda. At this dilution, the color change appears only in the drop, not on the paper which forms a neutral gray background; after 1 minute both the acid and alkaline drop show a definite change, to yellow and blue, respectively, compared with a drop of distilled water. (The water used for making up the caustic solution must be free from carbon dioxide.)

It is of theoretical interest to note the rearrangement which the dye molecule undergoes when changing from the yellow to the blue form. According to the theory of Hantzsch in its modification by Kolthoff (*3*), we have to assume that the dye in acid solution consists of the azo form:



In an alkaline medium this form, which is a pseudo acid, changes into the aci- or ionogen form:



This change causes the formation of two quinoid systems: Not only does the benzene ring rearrange to a *p*-quinoid form, but simultaneously an *o*-quinone is formed in the naphthalene ring. This conjugated system of two quinoid rings explains the color intensification of the dye in alkaline solution. It has been found that all dyes made by coupling diazotized 2,4-dinitroaniline with azo components in mineral acid solution show a similar color change. The 1-naphthol-3,6-disulfonic acid was selected as azo component because the dye derived from it shows the brightest colors and has the most favorable pH range of the dye series as far as it has been investigated.

LITERATURE CITED

(1) Kolthoff, I. M., "Indicators," p. 147, Wiley, 1926.
(2) *Ibid.*, pp. 224–5.
(3) *Ibid.*, p. 245.

RECEIVED October 10, 1933.

Upturn in 1933 Foreign Trade in Chemicals[1]

Otto Wilson, 3025 Fifteenth Street, Washington, D. C.

SELDOM in our history has any peace-time year witnessed more internal and external disturbances to foreign trade than 1933. It is encouraging, therefore, to find that the year's totals for both imports and exports of chemicals, just released by the Government, show a positive upward movement from the depressingly low levels of 1932. The gains were not excessive, and they left the record for the twelve months well below even the trade for 1931, but the movement was in the right direction and it enabled the chemical industry to close the year with a far more cheerful foreign trade outlook than seemed possible at the beginning. Export trade particularly was flushed with a new vigor at the year's end, December seeing much heavier sales abroad than any preceding month of 1933.

So far as the full year's totals were concerned, the returns seemed to fly in the face of one of the near-axioms of foreign trade economics. It is the common assumption that, when a country's currency depreciates, its export trade is proportionately stimulated and its import trade depressed. With the United States off the gold standard during practically ten months of the year, it was to be expected that the gain in exports would be much more pronounced than that in imports, since the foreign buyer of our wares would find his pound or franc worth much more in terms of dollars than before and hence would be able to buy more American goods; conversely, American importers would find their dollar worth less in pounds or francs and less potent in the purchase of foreign wares. The figures, however, reveal that the import pick-up was nearly three times as large in percentage as that in exports. As compared with 1932, last year's incoming trade in chemicals was 25 per cent heavier, and the outgoing trade 9 per cent. The result is to be ascribed, in part at least, to defensive measures against our exports adopted by foreign governments, such as tariff increases, quota restrictions regulating the flow of foreign trade, and particularly the operation of various plans for controlling exchange.

Table I. Import and Export Trade in Chemicals by Months

(In thousands of dollars)

Month	Imports 1932	Imports 1933	Exports 1932	Exports 1933
January	$4,794	$3,700	$6,459	$5,286
February	4,456	3,922	6,354	5,109
March	4,478	4,225	6,266	6,617
April	4,303	3,480	6,122	5,456
May	4,419	4,212	5,967	5,696
June	3,338	7,546	5,343	5,938
First 6 months	25,788	27,085	36,511	34,102
July	2,503	4,879	5,231	6,195
August	4,673	5,553	5,104	6,110
September	3,698	5,772	5,563	6,799
October	4,014	5,921	6,165	7,504
November	3,918	5,290	5,663	7,322
December	3,259	5,438	6,171	8,739
Last 6 months	22,065	32,853	33,897	42,669
Total for year	47,853	59,938	70,408	76,771

A study of the course of trade during the year, however, discloses that the depreciation of the dollar, despite these hindrances, did actually have much of the desired effect in promoting exports during the latter half of the year. That imports of chemicals showed an even greater rate of gain was due, apparently, to conditions outside of the chemical industry, since the country's general imports showed almost exactly the same six-month rate of increase as imports of chemicals. Increased purchasing power on the part of the public and a general desire among dealers and manufacturers to lay in stocks of foreign goods in fear of still higher prices were probably largely responsible for these import gains. The course of the year's trade and the general recovery beginning with June and July are shown in the month-by-month record of 1933 imports and exports as compared with the corresponding months of the preceding year (Table I).

Table I shows that up to June the 1933 totals for both imports and exports were below even the low figures of 1932. From June to December last year's totals were higher in each month, but the import trade of the last half-year showed a tendency to remain stationary or decline, while exports rose fairly steadily and reached their highest point in December, a promising augury for the present year.

While this general pick-up in business in chemicals is encouraging, our foreign trade has still a long distance to go before it reaches the levels of the prosperous years. Except for 1932, it touched its lowest point last year in the whole period since the war. Exports are barely half what they were in 1929 and imports are nearly 60 per cent less. In both departments of trade, however, the advance in chemicals is more notable than that of the general foreign commerce of the country, which showed a 9.5 per cent improvement in imports and a 4.5 per cent gain in exports as compared with 1932, and about a two-thirds decrease in both as compared with 1929. Table II shows the trade in chemicals in the last two years and in 1929 as compared with the total trade in those years.

Table II. Total U. S. Foreign Trade and Trade in Chemicals

(In thousands of dollars)

Year	Total Trade Imports	Total Trade Exports	Chemical Trade Imports	Chemical Trade Exports
1929	$4,399,000	$5,157,000	$144,062	$152,109
1932	1,323,000	1,576,000	47,852	70,408
1933	1,449,000	1,647,000	59,938	76,771
Increase 1932–33, %	9.5	4.5	25.3	9.0
Decrease 1929–33, %	67.0	68.1	58.4	49.5

CHEMICALS AND RELATED PRODUCTS

Recovery in the export trade was not at all uniform among the broader groups of chemicals, three of which, in fact, showed smaller returns in 1933 than in the year before. Coal-tar products led all the others and is now less than one-third below the level of five years ago. Industrial chemicals and specialties, paints, and explosives showed fair gains, but the trade in medicinals, fertilizers, and soaps fell short of that of the preceding year. In the incoming trade, on the other hand, medicinals and paints registered greater proportional gains than any other group. Paints and related products were purchased in much larger amounts and all others except the comparatively unimportant group, explosives, shared in the general upturn. Medicinals, industrial chemicals, and paints are leading on the road back to the prosperous trade of 1929. Table III gives the records of the great groups of chemicals over the last two years and in 1929.

Trade in the leading commodities of the various groups in 1933, and gains or losses as compared with 1932 and earlier years are detailed in the following pages.

---

[1] All 1933 figures are preliminary.

Table III. U. S. Foreign Trade in Chemicals by Great Groups

(In thousands of dollars)

Group	1929	1932	1933	Increase (+) or Decrease (−) 1932–1933 %	Increase (+) or Decrease (−) 1929–1933 %
IMPORTS					
Coal-tar products	$22,823	$9,158	$9,997	+9.2	−56.2
Medicinals and pharmaceuticals	6,421	2,530	3,605	+42.5	−43.9
Industrial chemicals	30,698	14,449	17,237	+19.3	−43.9
Pigments, paints, and varnishes	3,823	1,446	2,033	+40.6	−46.8
Fertilizers and materials	72,340	17,858	24,574	+37.6	−66.0
Explosives	960	371	244	−34.2	−74.6
Soap and toilet preparations	6,988	2,041	2,184	+7.0	−68.7
EXPORTS					
Coal-tar products	18,061	8,752	12,423	+41.9	−31.2
Medicinals and pharmaceuticals	21,283	10,027	9,816	−2.1	−53.9
Industrial chemical specialties	14,457	9,949	10,663	+7.2	−26.2
Industrial chemicals	28,149	14,958	16,802	+12.3	−40.3
Pigments, paints, and varnishes	29,111	10,366	11,834	+14.2	−59.3
Fertilizers and materials	20,441	8,653	8,269	−4.4	−59.5
Explosives, fuses, etc.	4,549	1,281	1,527	+19.2	−66.4
Soap and toilet preparations	16,061	6,422	5,436	−15.3	−66.2

Coal-Tar Products

The feature of the year's incoming trade in this group was the marked advance in our purchases of colors, dyes, stains, color acids, and color bases, which registered a total valuation of $6,061,000, a 27 per cent gain over the $4,688,000 of the previous year. The increased value was due both to heavier shipments, which rose from 4,245,000 to 5,020,000 pounds, and to higher prices, as indicated by an increase in the average valuation of imports from $1.14 to $1.20 per pound.[2] Ninety-five per cent of these imports come from Germany and Switzerland. Trade with both countries increased in 1933, Germany sending us $3,338,000 worth of these goods, a gain of about 30 per cent, and Switzerland $2,514,000, or about 36 per cent more.

Imports of dead or creosote oil continued to decline, amounting to 18,588,000 gallons with a valuation of $1,131,000, as against 29,300,000 valued at $2,647,000 in 1932. Coal-tar intermediates rose sharply in value, acids increasing from $202,000 to $234,000 despite a decrease in quantity from 833,000 to 333,000 pounds, and other intermediates rising from $584,000 to $1,327,000. Trade in coal-tar medicinals was reduced about 45 per cent, the valuation of $90,000 last year comparing with $164,000 in 1932.

Exports of coal-tar products made a handsome recovery in 1933, and the trade is now well along on the road back to its high levels of 1929 and 1930. In aggregate value of foreign sales the coal-tar group stood second among great groups of chemicals, being exceeded only by industrial chemicals. The 1933 total surpassed not only that of the preceding year but that of 1931 as well.

All classes of these products shared in the increased business. The greatest gain, however, came in the "all other" group, including all items not separately listed. These totaled $2,361,000 in value as against $1,033,000 in 1932. Among the listed articles the most notable increase was in the exports of benzene, of which 8,439,000 gallons valued at $1,594,000 were sent abroad in 1933 as compared with 3,421,000 valued at $612,000 in the previous year. There was considerable shifting about of the trade from its 1932 lines. Sales to France increased from 520,000 to 4,692,000 gallons, to Germany from 535,000 to 868,000 gallons, and to Japan from 374,000 to 1,309,000 gallons. The Netherlands, which was credited with 1,102,000 gallons in 1932, dropped out of the trade entirely, but its place was taken by the United Kingdom with 915,000 and Belgium with 365,000 gallons.

Crude coal-tar shipments registered an increase of nearly 50 per cent, rising from 400,000 to 591,000 barrels, with a proportionate gain in value. Coal-tar pitch enjoyed a smaller gain, from 188,000 to 199,000 tons, and from a total 1932 value of $2,125,000 to $2,414,000 last year. The largest class of coal-tar exports is that of colors, dyes, stains, and color lakes, in which a 1932 trade of 16,097,000 pounds with a value of $4,071,000 increased last year to 18,740,000 valued at $4,653,000. Creosote oil, with 137,000 gallons, showed a 20 per cent gain.

Medicinals and Pharmaceuticals

While the incoming trade in medicinals was piling up an increase of more than 40 per cent, the outgoing business was slightly dropping behind that of the year before. Heavier purchases were recorded in all the leading import items except menthol, which fell off from 351,000 pounds valued at $734,000 to 304,000 valued at $629,000. Quinine sulfate rose from 462,000 ounces valued at $154,000 to 1,639,000 valued at $558,000, and other cinchona bark derivatives from 321,000 ounces valued at $94,000 to 1,256,000 valued at $357,000. Preparations in capsules, pills, tablets, etc., not separately listed in 1932, were imported last year to a value of $643,000.

Medicinals and drugs exported from the United States consist of a wide variety of preparations, more than half of which, in point of value, consist of proprietary medicinal preparations. These dropped off slightly in 1933, the aggregate value of foreign sales reaching $4,956,000 as against $5,165,000 in the preceding year. The leading class of goods of this kind is that which includes tonics, blood purifiers, emulsions, and appetizers, of which $1,020,000 worth were sold last year as compared with $828,000 in 1932. Among other items returning an increased business in 1933 were plasters, $307,000 as against $295,000, in 1932; druggists' nonproprietary preparations, $2,799,000 as against $2,712,000; white mineral oil, $205,000 as against $201,000, although the quantity increased much more, from 321,000 to 414,000 gallons; serums and antitoxins for human use, $691,000 as against $629,000; and glandular products, etc., $621,000 as against $596,000. Items registering decreases included biologics for animal and veterinary use, $349,000 as against $390,000 in 1932; vaccines for human use, $137,000 as against $217,000; cold, cough, and bronchial proprietary preparations, $267,000 as against $306,000; and laxatives, purgatives, and cathartics, $593,000 as against $802,000.

Industrial Chemical Specialties

This group, comprising a number of articles largely for household and agricultural uses, appears only in the export trade. The popularity abroad of these American manufactures is attested by the fact that they have made more rapid progress in recovery than any other export group of chemicals. Sales last year showed a fair increase over the year before and brought the group's total business to about 75 per cent of the value of that done in the good year 1929.

Gains were not evenly distributed among the various manufactures last year, perhaps half of them showing losses as compared with 1932. Few large decreases or increases, however, were registered. The largest single item in point of value in the 1933 trade was household insecticides and exterminators, sold abroad to a total value of $1,189,000, a handsome gain of more than 40 per cent over the 1932 total of $827,000. Liquid preparations proved increasingly

---

[2] Average valuation figures, obtained by dividing the valuation of an import or export commodity by the quantity shipped, are not to be confused with prices, although they may be taken in a general way as an index to long-term price fluctuations. Valuations of imports, with few exceptions, represent foreign wholesale prices at port of shipment. Among the exceptions are coal-tar intermediates and finished products which are also made in the United States. In the past about half of the imports of finished coal-tar products have been included in the "American valuation" class. Aside from coal-tar chemicals all commodities of the chemical group take foreign valuation of imports. Valuations of exports are based on the export declarations of shippers and represent American values and prices.

popular last year over those in paste or powder form, and they comprised more than 90 per cent of the total. Rubber compounding agents (accelerators, retarders, etc.) showed sales of $819,000, a satisfactory return as compared with the $759,000 of the year before.

Third in point of value was petroleum jelly, shipments of which reached 11,766,000 pounds with a value of $669,000 as compared with 10,199,000 pounds valued at $611,000 in 1932. In point of bulk the leading commodity of this group was dextrin, or British gum. Exports in 1933 amounted to 14,600,000 pounds, a notable 50 per cent increase over the previous year's total of 9,750,000 pounds. The value, however, amounting to $486,000, represented only a 36 per cent increase.

Other important items showing increased business, with the percentage of gain in value over 1932, were: Cementing preparations, for repairing, sealing, and adhesive use, $430,000, an increase of 16 per cent; water softeners, purifiers, boiler-and-feed-water compounds, $255,000, an increase of 17 per cent; metal and stove polishes, $113,000, an increase of 7 per cent; shoe polishes and shoe cleaners, $271,000, an increase of 5 per cent; leather dressings and stains, $363,000, an increase of 7 per cent; floor wax, and wood and furniture polishes, $150,000, an increase of 15 per cent.

Decreases in this group were registered by agricultural insecticides, fungicides, etc., the value of which amounted to $775,000 as against $897,000 in 1932; baking powder, $579,000 against $616,000; textile specialty compounds, $219,000 against $240,000; tobacco extracts, $195,000 against $210,000; and automobile polishes, $137,000 against $148,000.

INDUSTRIAL CHEMICALS

Trade in both directions in these commodities, of special interest to manufacture, was brisker than in 1932. Our purchases and sales of these articles practically balance each other, the imports going slightly ahead of the exports last year. Table IV shows the quantities and values of the trade in full detail in the last two years.

PIGMENTS, PAINTS, AND VARNISHES

With an advance of over 40 per cent in our foreign purchases and a fair gain in sales abroad, our foreign trading in paints, varnishes, and related products was much more lively than in 1932. In general, imports have shown a better tendency to recover from the slump than exports, the outgoing trade being still about 60 per cent away from the 1929 movement.

Except for the small trade in varnishes every department of the import business in this group shared in the general gains. The leading class of these goods brought from abroad is paints, stains, and enamels, which more than doubled in value last year, imports totaling $506,000 as compared with $212,000 in 1932. Mineral earth pigments registered a total value of $750,000, a 45 per cent gain over the previous year, and chemical pigments $745,000, an increase of 9 per cent. Of the former, iron oxide and iron hydroxide were imported to the extent of 13,202,000 pounds, valued at $257,000, a gain of 36 per cent in quantity and 50 per cent in value; and ochers and siennas to the extent of 11,147,000 pounds with a value of $171,000, representing gains of 44 and 58 per cent, respectively. Lithopone and zinc pigments led the class of chemical pigments with 11,187,000 pounds valued at $313,000, an increase of 19 per cent in quantity and 15 per cent in value. Zinc oxide and leaded zinc oxide totaled 5,092,000 pounds, valued at $248,000, which compared with 5,345,000 valued at $242,000 the year before. Varnishes were brought in to the extent of 31,000 gallons valued at $33,000, practically the same in quantity but somewhat less in value than in 1932.

TABLE IV. IMPORTS AND EXPORTS OF INDUSTRIAL CHEMICALS

(In thousands)

	1932		1933	
IMPORTS	*Pounds*	*Value*	*Pounds*	*Value*
Acetylene, butylene, ethylene, and propylene derivatives	334	$37	1,052	$99
Acids and anhydrides:				
Acetic or pyroligneous	13,976	843	32,759	2,070
Arsenous (white arsenic)	13,768	358	21,167	513
Formic	139	8	249	13
Oxalic	265	13	121	6
Sulfuric (oil of vitriol)	1,498	11	2,049	19
Tartaric	1,818	298	597	104
All other	1,191	183	2,566	391
Alcohols, including fusel oil	....	11	....	11
Ammonium compounds, n. e. s.:[a]				
Chloride (muriate)	4,431	113	6,304	154
Nitrate	6,415	146	7,901	134
All other	215	10	830	71
Barium compounds	1,780	39	1,572	61
Calcium compounds	465	11	691	16
Cellulose products, n. e. s.:[a]				
Acetate	10	7	1	2
All other:				
Sheets more than 0.003 inch thick, and other forms	178	143	89	112
Sheets and strips, more than 1 inch wide, not over 0.003 inch thick	19	17	75	24
Cobalt oxide	226	220	569	414
Copper sulfate, free	3,243[b]	89[b]	....	...
Copper sulfate, dutiable				
Gross weight	64[c]	2[c]	54	2
Copper content	16[c]		13	
Glycerol, crude	5,382	204	6,205	233
Glycerol, refined	2,334	141	2,778	167
Iodine, crude	632	2,226	1,412	2,936
Lime, chlorinated, or bleaching powder	2,252	62	1,907	61
Magnesium compounds	11,479	146	11,433	161
Potassium compounds, n. e. s:[a]				
Carbonate	10,457	429	13,487	663
Chlorate and perchlorate	11,404	416	13,766	580
Cream of tartar	37	4	11	1
Cyanide	54	19	86	31
Hydroxide (caustic)	4,979	258	6,735	394
Argols, tartar, and wine lees	18,108	996	13,494	721
All other, n. e. s.[a]	2,692	168	3,114	213
Sodium compounds, n. e. s.:[a]				
Sulfate (salt cake), tons	61	644	89	885
Sulfate, anhydrous, tons	[d]	[d]	9	180
Chlorate	707	26	1,110	39
Cyanide	17,585	1,729	21,934	2,023
Ferrocyanide (yellow prussiate)	1,354	118	611	51
Nitrite	3	0.5	4	1
Phosphate (except pyrophosphate)	64	2	17	2
Other sodium compounds, n. e. s.[a]	....	484	....	393
Radium salts, grains (not in thousands)	141	479	179	576
Other industrial chemicals	....	2,508	....	2,709

(In thousands)

	1932		1933	
EXPORTS	*Pounds*	*Value*	*Pounds*	*Value*
Acids and anhydrides:				
Organic (exclusive of coal-tar acids)	359	63	447	84
Inorganic:				
Hydrochloric (muriatic)	6,410	97	3,235	56
Boric (boracic)	3,352	145	5,410	218
Other	9,621	320	9,405	373
Alcohols:				
Methyl, gallons	770	324	1,119	478
Butyl	1,507	138	4,891	440
Other	1,667	159	2,120	197
Acetone	4,404	318	3,508	255
Carbon disulfide	2,958	145	2,995	141
Formaldehyde (formalin)	2,103	101	2,373	121
Citrate of lime	6,245	464	8,036	497
Other organic chemicals	7,760	1,075	9,368	1,280
Nitro- or acetocellulose solutions, collodion, etc.	2,018	373	2,526	477
Aluminum sulfate	43,099	463	56,540	544
Other aluminum compounds	653	59	853	70
Calcium carbide	2,287	93	2,310	84
Calcium chloride	35,494	378	31,371	312
Copper sulfate (blue vitriol)	4,133	115	2,749	93
Hydrogen peroxide (or dioxide)	593	88	575	91
Potassium compounds (not fertilizers)	1,773	241	2,550	302
Sodium compounds:	410,582	7,221	446,241	7,739
Dichromate and chromate	6,178	329	9,702	486
Cyanide	839	114	457	66
Borate (borax)	179,282	2,678	175,353	2,498
Silicate (water glass)	50,343	401	43,985	320
Soda ash	27,595	460	56,883	750
Sal soda	5,723	85	3,931	60
Bicarbonate (acid soda or baking soda)	14,019	252	14,936	246
Hydroxide (caustic soda) in drums	110,977	2,360	121,322	2,611
Sodium phosphate (mono-, di-, or tri-)	5,686	168	7,778	183
Other sodium compounds	9,940	375	11,894	520
Tin compounds	582	90	105	35
Gases, compressed, liquefied, and solidified:				
Ammonia, anhydrous	999	134	1,146	149
Chlorine	6,383	161	13,418	277
Other gases, n. e. s.[a]	5,178	348	16,426	412
Other industrial chemicals	....	1,845	....	2,077

[a] Not elsewhere specified.
[b] January 1 to June 20.
[c] June 21 to December 31.
[d] Not separately stated.

A large advance in bulk and a smaller advance in value raised the export shipments of carbon black to 152,286,000 pounds, valued at $5,552,000, and left it not only the outstanding export item in this class of goods but one whose value was almost as great as that of all others combined. In 1932 exports stood at 100,072,000 pounds, valued at $4,436,000. This trade is scattered among most of the countries of the world, with the United Kingdom usually the largest buyer and France and Germany taking considerable amounts.

Ready mixed paints, stains, and enamels comprised about one-third in value of the rest of our exports of paints and related materials. They registered a small gain over 1932, shipments amounting to 1,202,000 as against 1,045,000 pounds, and total value to $2,147,000 as against $2,015,000. In the outgoing trade in nitrocellulose lacquers, pigmented lacquers and thinners enjoyed notable increases but clear lacquers were reduced. Exports of pigmented lacquers were 337,000 gallons having a value of $813,000, compared with 226,000 with a value of $604,000 in 1932; clear lacquers were 61,000 gallons valued at $117,000, against 79,000 valued at $160,000; and thinners 318,000 gallons valued at $281,000 against 205,000 valued at $220,000. Mineral earth pigments, nearly half of which consisted of forms of iron oxide, were sold abroad to the extent of 21,608,000 pounds, a 40 per cent gain, valued at $352,000, an increase of about 23 per cent. Other exports last year included kalsomine dry paints, $227,000, slightly less than in 1932; bituminous paint, liquids, and plastic, $339,000, a 27 per cent gain; paste paint, $198,000, a 22 per cent loss; and varnishes, oil or spirit, including liquid driers, $391,000, an increase of about 9 per cent.

Fertilizers and Fertilizer Materials

Increased activity in this group of commodities in 1933 was confined largely to the import trade and to two or three commodities among the exports. The out-going trade as a whole suffered a slight decrease, but shipments to the United States from foreign countries were more than a third heavier in the aggregate than in 1932.

The gain in imports was due to much heavier shipments of nitrogenous and potash fertilizers. Phosphate imports showed a small decline, amounting to 61,000 tons in 1933 as against 67,000 the year before. The value also fell off from $942,000 to $919,000. About one-half of these imports consist of bone ash, dust, and meal, and animal carbon fertilizers, which amounted in 1933 to 29,000 tons, a 5 per cent loss, valued at $520,000, an increase of about 2 per cent.

Nitrogenous fertilizer imports rose from 493,000 tons with a value of $10,361,000 in 1932 to 689,000 with a value of $13,136,000 in 1933. About 50 per cent of the whole consist of ammonium-sulfate imports, which reached a total of 351,000 tons with a value of $6,179,000 last year as compared with 307,000 tons with a value of $5,410,000 the year before. Sodium nitrate recovered somewhat from the tremendous slump in imports in 1932, when our purchases of the Chilean product amounted to only 50,000 tons, valued at $1,472,000. This trade, once so flourishing, as late as 1931 furnished us with more than half a million tons of nitrate, worth over $21,000,000, and within a little more than a decade it had registered a value in one year of more than three times that figure. The gain in 1933, when 123,000 tons valued at $2,343,000 came in, thus seems almost inconsiderable although in point of value it was nearly 60 per cent. The average import valuation last year stood at $19 as against $29 in 1932. Calcium cyanamide, with 63,800 tons, registered a small gain of about 1300 tons over the preceding year, but the total value, $1,416,000, was some 13 per cent less. Imports of guano more than doubled last year, amounting to about 60,000 tons as against 1932 shipments of 24,000 tons, and being valued at $1,118,000 as against $490,000.

Potash fertilizers made a smart recovery from the low 1932 levels, all classes showing good gains. All told, we purchased 406,000 tons of these fertilizers from abroad last year and paid $9,238,000 for them. In 1932 the total shipments were 274,000 tons and their value $6,542,000, last year's trade increasing 48 per cent in quantity and 41 per cent in value. Imports of the chief classes of these goods for the two years are shown in Table V.

Table V. Imports of Potash Fertilizers

(In thousands)

	1932		1933	
	Tons	*Value*	*Tons*	*Value*
Chloride, crude	78	$2795	106	$3792
Kainite	49	457	102	968
Manure salts	101	1255	113	1329
Sulfate, crude	28	1202	59	2262
Nitrate, crude (saltpeter)	17	831	26	880
Other potash-bearing substances	[a]	3	[b]	7
Total	273	6543	406	9238

[a] 351 tons. [b] 449 tons.

The slight falling off in exports of fertilizers was due almost entirely to a decrease in nitrogenous fertilizers, as phosphatic and potassic materials were sent abroad in considerably larger quantities. Nitrogenous fertilizers, which in 1932 totaled 191,000 tons with a value of $4,922,000, last year reached only 117,000 with a value of $2,729,000. Ammonium sulfate exports of 14,000 tons valued at $362,000 compared with 15,000 valued at $408,000 in the preceding year, and those of other nitrogenous chemical materials to a value of $2,152,000 as compared with $4,357,000. Potassic materials amounted to 25,000 tons and were valued at $910,000, an immense increase over 1932 when only 1816 tons valued at $70,000 were sent abroad. The increase was due to very heavy shipments to Japan, especially in the earlier part of the year, and to Canada.

The livelier trade in phosphate fertilizer materials is shown by the export figures in the last two years (Table VI).

Table VI. Exports of Phosphate Materials

(In thousands)

	1932		1933	
	Tons	*Value*	*Tons*	*Value*
Phosphate rock:				
High-grade hard rock	66	$406	42	$295
Land pebble	547	2390	787	3249
Superphosphate	24	259	35	334
Other phosphate materials	1	60	3	150
Total	638	3115	867	4028

Explosives, Fuses, etc.

Foreign purchases under this head, as usual, consisted almost wholly of firecrackers, the value of which last year was $220,000. In 1932 it was $346,000. The chief export item was dynamite, of which we sold abroad 5,941,000 pounds valued at $777,000, which compares with 4,607,000 valued at $600,000 the year before. Safety fuses valued at $298,000, an 18 per cent gain over 1932, and blasting caps at $167,000, a 36 per cent gain, were the chief other exports.

Soap and Toilet Preparations

About half of the imports under this classification last year consisted of perfume materials, which totaled $1,022,000 in value, and half of the remainder consisted of perfumery, bay rum, and toilet water, $511,000. In 1932 these items stood at $873,000 and $342,000, respectively. Cosmetics, powders, creams, etc., were imported to a value of $206,000, the 1932 figure being $242,000. Imports of soaps, of which castile was most important, totaled $441,000, against $578,000 the year before.

Foreign sales under this head, as usual, included a rather wide variety of commodities, the largest single one being dental creams. Exports of these goods amounted to 1,268,000 pounds valued at $1,001,000, a slight decline from 1932. Among the soaps, laundry soap with exports valued at $621,000 and toilet soap, $716,000, were most important. The year before, these articles were sold to the extent of $1,215,000 and $708,000, respectively. Among the other considerable items were talcum powder, in packages, $447,000, an 11 per cent gain; hair preparations, $348,000, a 7 per cent gain; scouring soaps, bricks, pastes, and powders, $243,000, a 7 per cent decrease; and cold creams, $202,000, practically the same as in 1932.

MATERIALS RELATED TO CHEMICAL INDUSTRIES

Many manufacturers will be interested in other commodities than those mentioned above, which are included in the Government's statistical classification of Chemicals and Related Products. For a number of these articles the 1933 foreign trade record is presented below.

Mineral Oils

Imports of petroleum and products were greatly reduced in 1933 while exports were only slightly under those of the previous year in value. Comparative figures for trade in various classes of these oils for the two years are given in Table VII.

Table VII. Imports and Exports of Petroleum and Products

(In thousands)

	1932		1933	
	Barrels	*Value*	*Barrels*	*Value*
IMPORTS				
Petroleum and products, total	...	$60,631	...	$25,893
Petroleum, crude	44,700	30,424	31,924	17,718
Advanced and refined oils:	30,227	29,241	13,990	7,212
Fuel oil, including topped petroleum	21,724	11,401	13,933	6,839
Unfinished distillates	12	116	19	157
Finished light products	8,394	17,286	25	90
Illuminating oil	78	116	9	55
Lubricating oil	19	322	4	71
EXPORTS				
Petroleum and products, total	...	208,381	...	200,016
Petroleum, crude	27,391	27,106	36,584	31,979
Natural gasoline	308	533	1,657	3,395
Refined oils:	69,348	168,139	61,419	151,269
Gasoline, naphtha and other finished light products	33,823	79,081	25,996	57,520
Illuminating oil (kerosene)	10,867	23,732	8,764	19,209
Gas oil and distillate fuel oil	8,118	9,295	10,232	12,348
Residual fuel oil	9,713	6,877	8,223	5,962
Lubricating oil	6,732	48,282	8,111	55,389
Fuel or bunker oil for vessels in foreign trade (not included in exports)	38,152	29,392	32,272	27,103

The heavy decreases in imports are to be ascribed largely if not entirely to the new duty on petroleum and its products which went into effect June 21, 1932, and applied to all imports throughout 1933.

Sulfur

Last year saw a considerable increase in the exports of sulfur. Crude sulfur, in lump form, was sold abroad to the extent of 523,000 tons, valued at $9,878,000, which compares with 353,000, valued at $7,179,000 in 1932. Crushed, ground, refined, and sublimed sulfur and flowers of sulfur totaled 19,629,000 pounds in 1933, with a value of $317,000, as against 16,285,000 valued at $266,000 the year before.

Vegetable and Essential Oils

Imports of edible vegetable oils and fats were slightly higher in value last year, $7,806,000 as compared with $7,687,000. The great bulk of these imports consists of olive oil, of which 71,963,000 pounds were brought in in 1933 as against 74,274,000 in 1932, the valuation also falling from $6,975,000 to $6,649,000. Sunflower-seed oil, valued at $748,000, was the leading other item, imports showing a great advance from the $411,000 of 1932.

Among the inedible vegetable oils, coconut oil, palm oil, and tung oil are outstanding. All three showed notable gains last year. Coconut oil remained in the lead with 316,078,000 pounds, which compares with 249,117,000 in 1932. The total value for 1933 was $8,556,000 and that for the year before $7,619,000. Palm oil imports registered 287,483,000 pounds valued at $7,001,000 in 1933 as against 217,167,000 valued at $5,998,000 the previous year, and tung oil 118,760,000 pounds valued at $4,833,000 as against 75,922,000 valued at $3,434,000.

In the export trade refined cottonseed oil led the edible vegetable oils with sales of 9,292,000 pounds, valued at $561,000, a loss of 15 per cent in quantity and about the same in value. Crude cottonseed oil, with a value of $778,000, representing a 46 per cent decrease, was second only to coconut oil among the inedible vegetable oils. Coconut oil, valued at $798,000, was slightly higher than in 1932.

Imports of essential oils in the last two years are shown in Table VIII.

Table VIII. Imports of Essential Oils

(In thousands)

	1932		1933	
	Pounds	*Value*	*Pounds*	*Value*
Cassia and cinnamon	326	$158	410	$200
Geranium	145	463	128	480
Attar of roses, ounces	15	105	33	205
Bergamot	40	73	75	91
Citronella and lemon grass	1508	483	1865	663
Lavender and spike lavender	212	228	270	385
Lemon	167	123	271	161
Orange	114	112	149	110
Sandalwood	5	19	3	13
Lime	[a]	[a]	41	215
All other	2962	982	2853	887
Total		2746		3410

[a] Not separately stated.

Peppermint and pine oils are the chief essential oils sold abroad by American exporters. Both showed good gains in value in 1933, peppermint oil reaching 235,000 pounds valued at $567,000 as against 262,000 valued at $455,000 in 1932, and pine oil 841,000 pounds valued at $471,000 as against 435,000 valued at $246,000.

Dyeing and Tanning Materials

Out of a total import value of $4,961,000 for dyeing and tanning materials in 1933, slightly more than half was credited to quebracho extract. A total of 121,871,000 pounds with a value of $2,526,000 were brought in, a marked gain over the previous year's imports of 105,388,000 valued at $1,819,000. Quebracho wood, $313,000, and logwood, $335,000, were the leading raw materials for the manufacture of dyeing and tanning agents, and showed large increases of about 150 and 75 per cent, respectively. Logwood extract (including hematin crystals) valued at $105,000, and chestnut extract, $132,000, were the only two important items listed separately among the exports of dyeing and tanning materials, the total of which amounted to $1,630,000 last year as compared with $1,483,000 in 1932.

Rubber

Higher prices last year brought the total value of our imports of crude rubber up to a point more than 40 per cent above that of the preceding year while the total quantity showed little increase. The 1933 figures stood at 938,340,000 pounds with a value of $45,868,000 while those of the year before were 928,857,000 pounds with a value of $32,538,000. The growing interest in balata was reflected in 1933 imports amounting to 3,716,000 pounds valued at $2,262,000, whereas in 1932 only 1,585,000 pounds valued at $147,000 were imported.

Gums, Resins, and Naval Stores

As usual, crude chicle took first place on the list of imports of this class of goods. Shipments of 4,066,000 pounds were valued at $1,081,000, a falling-off of 18 per cent in amount and 46 per cent in value. Shellac, with a value of $972,000, showed a 35 per cent loss and crude lac, $873,000, a 14 per cent loss. Crude natural camphor was imported to the extent of 1,989,000 pounds valued at $411,000, an increase of about 10 per cent in quantity and a decrease of 20 per cent in value; natural refined camphor, 1,630,000 pounds valued at $490,000, gained 57 per cent in quantity and 37 per cent in value; and synthetic camphor, 1,460,000 pounds valued at $406,000 in 1932, dropped to 880,000 valued at $216,000 last year.

Exports of naval stores, gums, and resins more than recovered the ground they lost in 1932, the total value rising $14,714,000, whereas in 1932 it stood at $11,587,000 and in 1931 at $14,304,000. Trade in the various articles in the last two years is shown in Table IX.

Table IX. Exports of Naval Stores, Gums, and Resins

(In thousands)

	1932		1933	
	Quantity	*Value*	*Quantity*	*Value*
Naval stores:				
Gum rosin, barrels	938	$5,345	994	$6,540
Wood rosin, barrels	160	911	219	1,324
Gum spirits of turpentine, gallons	10,940	4,410	13,388	5,781
Wood turpentine, gallons	529	229	851	343
Tar and pitch of wood, barrels	6	56	7	65
Other gums and resins, pounds	3,682	636	4,248	661
Total .		11,587		14,714

Received February 10, 1934.

Tabular Method of Reading Arsenic Strips

Bertram D. Thomas, University of Washington, Seattle, Wash.

Traces of arsenic in such common foodstuffs as fruit are usually determined by some modification of the Gutzeit evolution method. The sample after appropriate treatment is placed in an evolution flask and treated with stannous chloride to reduce arsenates to arsenites and with zinc and hydrochloric acid to reduce all the arsenic to arsine. This is swept out of the flask by the excess of hydrogen which is formed at the same time, and passed over strips of paper impregnated with mercuric bromide. The arsine colors the strip, and by using suitable standards the amount of arsenic in the sample may be estimated by measuring the length of the stain produced on the strip and comparing with the lengths of the standard stains.

The comparison is usually effected by plotting the values of the standards and the corresponding stain lengths on coordinate paper, passing a smooth curve through the points, and reading the values of the samples graphically by interpolating along the curve.

This is a somewhat laborious process; and since it must be repeated for every set of standards, considerable time is required for the mere mechanical details of plotting the data. The method also has the additional disadvantage, common to most graphical methods, of allowing choice as to the way the curve is drawn. More than one curve may usually be drawn through a set of points, and the differences are sometimes considerable.

Where a large number of determinations are being made, the results may be obtained much more rapidly and probably more accurately by means of tables calculated for particular sets of standards. By examination of a large number of determinations it has been found that while the lengths of a given standard vary widely from set to set, the relative lengths of the various standards in the sets are quite constant. The sum of the lengths of the standards is sufficient to characterize the curve and therefore the table necessary to calculate the values of the samples.

Suppose values of the standards are taken containing 0.01, 0.02, 0.03, and 0.04 mg. of arsenic trioxide. When these are evolved in the ordinary manner, the lengths of the stains of a particular set are found to be 8.5, 13.5, 17.0, and 20.0 mm., respectively; and the total length, 59 mm. This total length suffices to determine the table from which the results may be read. Practically it has been found that about 25 tables are necessary to cover a variation in the total length of the standards from 45 to 70 mm. These may be arranged to permit interpolation for fractions of a millimeter, depending upon the requirements and usage of the laboratory and, if desired, to read directly in grains per pound if spray residues are being determined on fruit. Average values of the lengths of the standards are given with each table to permit immediate detection of a gross error.

Careful comparison of results calculated by the graphical method and those taken from the tables has shown that the differences are usually less than 5 per cent. Greater deviations can always be attributed to faulty standards, which are made immediately apparent by the average values given in the table, or to an actual choice in the curve drawn through the points. In this latter case the tables are much more reliable. Even in the case of a relatively large error in one of the lower standards, the tables still seem to give results within the experimental error of the Gutzeit method (*1*).

The tables must be calculated to fit the particular conditions under which the determinations are made, although these conditions may vary quite widely without producing appreciable change in the relative values of the standards. The tables may be easily computed by using the data which accumulate during the determinations themselves, preferably by plotting the arsenic equivalent of particular strip lengths against the total length of the standards in the set from which the strip is taken and interpolating values for the tables. The 5-, 10-, 15-, and 20-mm. lengths are sufficient to permit the rest of the values to be interpolated. It is desirable, of course, to have as many sets of standards available as possible in plotting the curves.

Literature Cited

(1) Barnes and Murray, Ind. Eng. Chem., Anal. Ed., 2, 29 (1930).

Received December 8, 1933.

MARKET REPORT—FEBRUARY, 1934

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, FEBRUARY 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

NEWER CHEMICALS

Acetaldehyde, drums, lc-l., wks.	lb.	.16
Acetaldol, 50-gal. drums	lb.	.27
Acetylene tetrachloride, *see* Tetrachloroethane		
Acid, abietic	lb.	.07
Adipic	lb.	.72
Furoic, tech., drums	lb.	.35
Linoleic	lb.	.16
Naphthenic, drums	lb.	.10
Sebacic, tech.	lb.	.58
Ammonium linoleate, drums	lb.	.12
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, c/l.	lb.	.26
Dichloroethyl ether, 50-gal. drums, c/l.	lb.	.21
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.	.15
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.	.05½
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%, tanks	lb.	.15
Cellosolve, *see* Ethylene glycol monomethyl ether		
Methyl hexyl ketone, pure	lb.	1.20
Paraldehyde, 110–55 gal. drums, c/l.	lb.	.16
Phosphorus oxychloride, 175 cyl.	lb.	.20
Potassium abietate	lb.	.06
Sodium abietate	lb.	.06
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

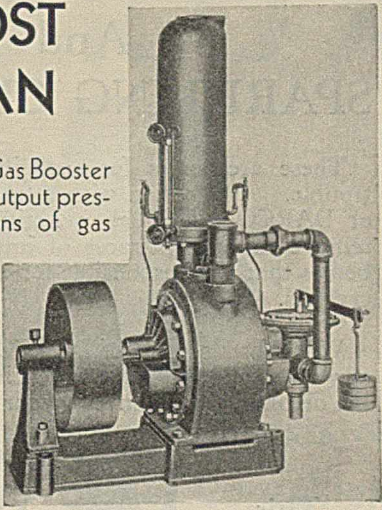
Acetanilide, U. S. P., powd., bbls.	lb.	.26
Acetic anhydride, 92–95%, cbys.	lb.	.21
Acetone, drums, wks., c/l.	lb.	.11
Acetphenetidin, bbls.	lb.	1.30
Acid, acetic, 28%, c/l., bbls.	100 lbs.	2.91
56%, c/l., bbls.	100 lbs.	5.50
Glacial, c/l., bbls.	100 lbs.	10.02
Glacial, U. S. P., c/l., carboys	100 lbs.	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.	.15½
Cinnamic, bottles	lb.	3.25
Citric, U. S. P., cryst., bbls.	lb.	.28
Cresylic, pale, drums	gal.	.50
Formic, 90%, cbys., N. Y.	lb.	.11
Gallic, U. S. P., bbls.	lb.	.77
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.	.11⅞
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.	.18
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.	.25½
Tungstic, kegs	lb.	1.40
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	4.15½
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		
Aldol, 95%, drums, c/l.	lb.	.21
Alpha-naphthol, bbls.	lb.	.65
Alpha-naphthylamine, bbls.	lb.	.33
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.00
Chrome, casks, wks.	100 lbs.	7.00
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.	.17
Aluminum sulfate, comm'l, bags, wks.	100 lbs.	1.35
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.	.15¼
Bromide, bbls.	lb.	.39
Carbonate, tech., casks	lb.	.08
Chloride, gray, bbls.	100 lbs.	5.50
Lump, casks	lb.	.10½
Iodide, 25-lb. jars	lb.	4.30
Nitrate, tech., cryst., bbls.	lb.	.08½
Oxalate, kegs	lb.	.24
Persulfate, cases	lb.	.20
Phosphate, dibasic, tech., bbls.	lb.	.08½
Sulfate, bulk, wks.	ton	25.00
Amyl acetate, tech., from pentane, tanks, delivered	lb.	.135
Aniline oil, drums	lb.	.16½
Anthracene, 80–85%, casks, wks.	lb.	.75
Anthraquinone, subl., bbls.	lb.	.45
Antimony, metal	lb.	.07¼
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.	.44
Red, kegs, cases	lb.	.14
White, c/l., kegs	lb.	.04½
Asbestine, bulk, c/l.	ton	15.00
Barium carbonate, bbls., bags, wks.	ton	45.00
Chloride, bbls., wks.	ton	74.00
Dioxide, drs., wks.	lb.	.12
Hydroxide, bbls.	lb.	.05
Nitrate, casks	lb.	.08½
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.	.20½
Benzoyl chloride, drums	lb.	.40
Benzyl acetate, F. F. C., bottles	lb.	.75
Alcohol, drums	gal.	.85
Chloride, tech., drums	lb.	.30
Beta-naphthol, bbls.	lb.	.24
Beta-naphthylamine, bbls.	lb.	.58
Bismuth, metal, cases	lb.	1.30
Bismuth, nitrate, 25-lb. jars	lb.	1.20
Oxychloride, boxes	lb.	2.95
Subnitrate, U. S. P., 25-lb. jars	lb.	1.40
Blanc fixe, dry, bbls.	ton	70.00
Bleaching powder, drums, wks.	100 lbs.	1.90
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, bags	lb.	.018
Bordeaux mixture, bbls.	lb.	.10½
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

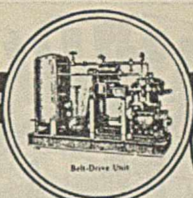
Cadmium sulfide, boxes	lb.	.60
Caffeine, U. S. P., 5-lb. cans	lb.	1.85
Calcium acetate, bags	100 lbs.	3.00
Arsenate, bbls.	lb.	.06¾
Carbide, drums	lb.	.05½
Chloride, drums, wks., flake	ton	19.50
Cyanide, 100-lb. drums	lb.	.30
Nitrate, bags, 15% N	ton	25.50
Phosphate, monobas., bbls.	lb.	.07½
Tribas., bbls.	lb.	.11
Calcium carbonate, tech., bags,	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl.	lb.	.06½
Camphor, Jap., slabs	lb.	.55
Carbazole, bbls.	lb.	.75
Carbon, activated, drums	lb.	.08
Carbon bisulfide, drums	lb.	.051
Carbon black	lb.	.04†
Carbon dioxide, liq. cyl.	lb.	.06
Carbon tetrachloride, drums	lb.	.05¼
Casein, stand. gr., bbls.	lb.	.12
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.	1.85
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.	1.25
Cod liver oil, bbls.	bbl.	28.00
Copperas, c/l., bulk	ton	14.50
Copper, metal, elec.	100 lbs.	8.25
Copper carbonate, bbls., 52/54%	lb.	.15½
Chloride, bbls.	lb.	.17
Cyanide, drums	lb.	.39
Oxide, red, bbls.	lb.	.12½
Sulfate, c/l., bbls.	100 lbs.	3.75
Cotton, soluble, bbls.	lb.	.40
Cream tartar, bbls.	lb.	.17½
Cyanamide, bulk, N. Y.	Ammonia unit	1.07½
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.	.29
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, tech., drums	lb.	.17
Dinitrochlorobenzene, bbls.	lb.	.14½
Dinitronaphthalene, bbls.	lb.	.34
Dinitrophenol, bbls.	lb.	.23
Diphenylamine, bbls.	lb.	.31
Diphenylguanidine, bbls.	lb.	.36
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.70
Ether, nitrous, bot.	lb.	.75
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.	1.10
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerine, c. p., drums	lb.	.11½
G salt, bbls.	lb.	.42
Hexamethylenetetramine, tech., drums	lb.	.37
Hydrogen peroxide, 25 vol., bbls.	lb.	.05½
Hydroquinone, kegs	lb.	1.20
Indigo, 20%, paste, bbls.	lb.	.12
Iodine, crude, 200-lb. kgs.	kilo	15s. 1d.
Iodine, resubl., jars	lb.	2.25
Iron acetate, liq., 17°, bbls., c/l.	lb.	.03
Kieselguhr, bags	ton	50.00
Lead, metal, N. Y.	100 lbs.	4.00
Lead acetate, bbls., white	lb.	.11
Arsenate, bbls.	lb.	.10
Oxide, litharge, bbls.	lb.	.06¾
Peroxide, drums	lb.	.20
Red, bbls.	lb.	.07¾
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, calcined, 500-lb. bbls., wks.	ton	60.00
Magnesium, metal, wks.	lb.	.30
Magnesium carbonate, bags	lb.	.06½
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.	.82
Mercury flasks, 76 lbs.	flask	70.00
Meta-nitroaniline, bbls.	lb.	.67
Meta-phenylenediamine, bbls.	lb.	.82
Meta-tolylenediamine, bbls.	lb.	.67
Methanol, pure, synthetic, drums, delivered, c/l.	gal.	.37½
Tanks, delivered	gal.	.35½
Methyl acetone, drums	gal.	.54½
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.45
Michler's ketone, bbls.	lb.	2.50
Naphthalene, flake, bbls.	lb.	.06
Nickel, metal	lb.	.35
Nickel salt, single, bbls.	lb.	.11½
Double, bbls.	lb.	.11½
Niter cake, bulk	ton	11.50
Nitrobenzene, drums	lb.	.09
Oil, castor, No. 1	lb.	.10¼
China wood, bbls.	lb.	.07¾
Coconut, Ceylon, tanks	lb.	.03⅝
Cod, N. F., bbls.	gal.	.40
Corn, crude, tanks, mills	lb.	.04⅛
Cottonseed, crude, tanks	lb.	.03½
Linseed, bbls.	lb.	.095
Menhaden, crude, tanks	gal.	.15
Neat's-foot, pure, bbls.	lb.	.13
Oleo, No. 1, bbls.	lb.	.06¼
Olive oil, denat., bbls.	gal.	.82
Foots, bbls.	lb.	.06½
Palm, Lagos, casks	lb.	.03⅞
Peanut, crude, tanks	lb.	.04¼
Perilla, bbls.	lb.	.08¼
Rapeseed, bbls.	gal.	.41½
Red, bbls.	lb.	.07
Soy bean, crude, tanks	lb.	.06
Sperm, 38°, bbls.	lb.	.108
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.	.05½
Ortho-toluidine, bbls.	lb.	.14
Para-aminophenol, kegs	lb.	.78
Para-dichlorobenzene	lb.	.16
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.	.35
Para-phenylenediamine, bbls.	lb.	1.15
Para-toluidine, bbls.	lb.	.56
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.	.14½
Platinum, metal	oz.	36.00
Potash, caustic, drums	lb.	.07¼
Potassium acetate, kegs	lb.	.27
Bicarbonate, casks	lb.	.07½
Bichromate, casks	lb.	.08⅛
Binoxalate, bbls.	lb.	.14
Bromide	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.07
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.	.18½
Prussiate, red, casks	lb.	.39
Yellow, casks	lb.	.18
Titanium oxalate, bbls.	lb.	.32
Pyridine, drums	gal.	1.25
Resorcinol, tech., kegs	lb.	.65
Rochelle salt, bbls., U. S. P.	lb.	.12½
R salt, bbls.	lb.	.44
Saccharin, cans	lb.	1.70
Salt cake, bulk	ton	13.00
Saltpeter, gran., bbls.	lb.	.06
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot.	oz.	.31⅝
Soda ash, 58%, light, bags, contract, wks.	100 lbs.	1.23
Soda, caustic, 76%, solid, drums, contract, wks.	100 lbs.	2.60
Sodium acetate, bbls.	lb.	.05
Benzoate, bbls.	lb.	.45
Bicarbonate, bbls.	100 lbs.	1.85
Bichromate, casks	lb.	.06⅛
Bisulfite, bbls.	lb.	.03
Bromide, bbls., U. S. P.	lb.	.35
Chlorate, kegs	lb.	.05¾
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.15½
Fluoride, bbls.	lb.	.07½
Metallic, drums, 12¼-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.	1.315
Nitrite, bbls.	lb.	.07¼
Perborate, bbls.	lb.	.17
Peroxide, cases	lb.	.20
Phosphate, trisodium, bbls.	100 lbs.	2.60
Phosphate, disodium, bags	100 lbs.	2.10
Picramate, kegs	lb.	.67
Prussiate, bbls.	lb.	.11½
Silicate, drums, tanks, 40°	100 lbs.	.80
Silicofluoride, bbls.	lb.	.05
Stannate, drums	lb.	.34
Sulfate, anhyd., bbls.	100 lbs.	2.20
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.	.09½
Sulfur, bulk, mines, wks.	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
Sulfur dioxide, commercial, cyl.	lb.	.07
Sulfuryl chloride, drums	lb.	.10
Thiocarbanilid, bbls.	lb.	.25
Tin	lb.	.52
Tin tetrachloride, anhydrous, drums, bbls.	lb.	.25½
Oxide, bbls.	lb.	.55
Titanium dioxide, bbls., wks.	lb.	.17¼
Toluene, tanks	gal.	.30
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.58
Triphenyl phosphate, bbls.	lb.	.37
Tungsten, powder	lb.	1.65
Urea, pure, cases	lb.	.15
Whiting, bags	ton	7.00
Xylene, 10°, tanks, wks.	gal.	.29
Xylidine, drums	lb.	.36
Zinc, metal, E. St. Louis	100 lbs.	4.25
Zinc ammonium chloride, bbls.	lb.	.05
Chloride, granulated, drums	lb.	.05⅜
Oxide, Amer., bbls.	lb.	.05¾
Stearate, bbls.	lb.	.18
Zinc dust, bbls., c/l.	lb.	.0625

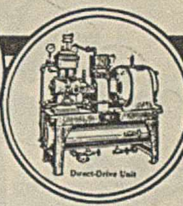
---

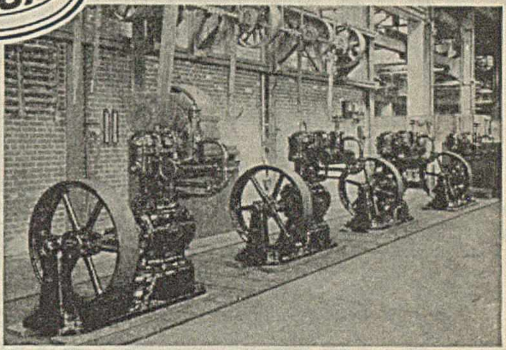
† This is the approximate F. O. B. shipping point price. Quotations are now all on a delivered basis and vary with the section.

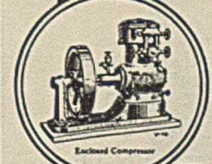
* F. O. B. destination.

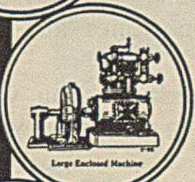



Belt-Drive Unit

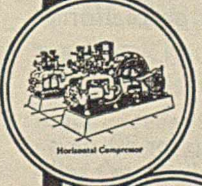

Direct-Drive Unit

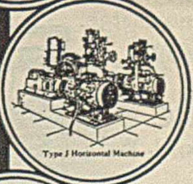


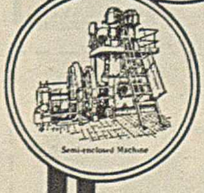

Enclosed Compressor

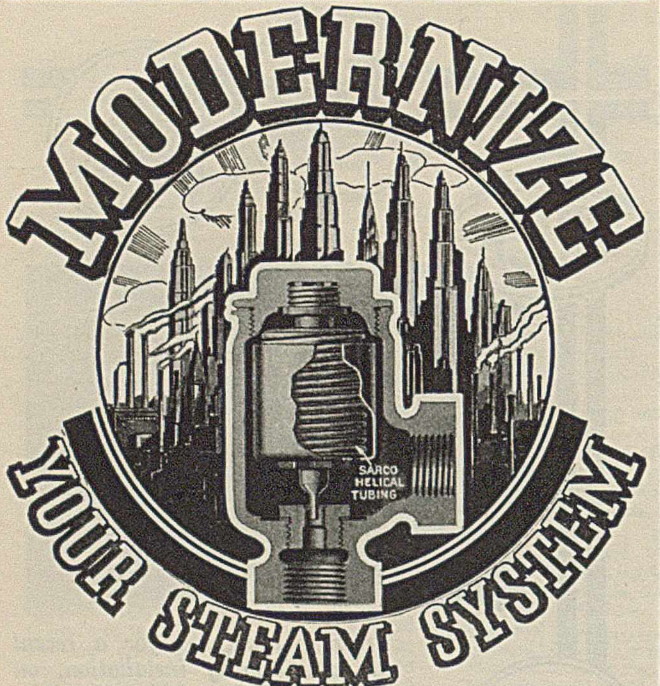

Large Enclosed Machine


Carbon-Dioxide Machine

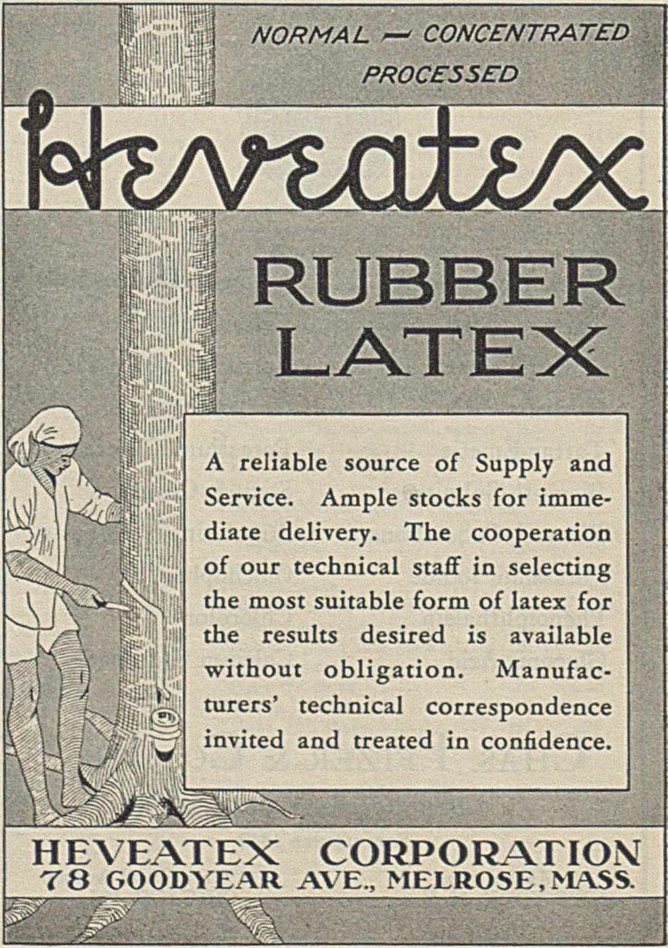

Horizontal Compressor


Type J Horizontal Machine


Semi-enclosed Machine


MODERNIZE
SARCO HELICAL TUBING
YOUR STEAM SYSTEM


Protect Your Pipe with SARCO PIPE SAVERS



VIBROX

Will Cut Your Packing Costs on Barrels--Bags--Other Containers

The VIBROX—a real cost reducing unit—operates continuously—no starting or stopping—no clutches to throw. Eliminates manual jiggling or shaking—packs the material as it falls into the container. No matter what size or type of container you are using—from 5 lbs. upward—there is a standard VIBROX that will lower your operating costs. Why not get the facts? Write for Bulletin V-26.

B. F. GUMP CO.

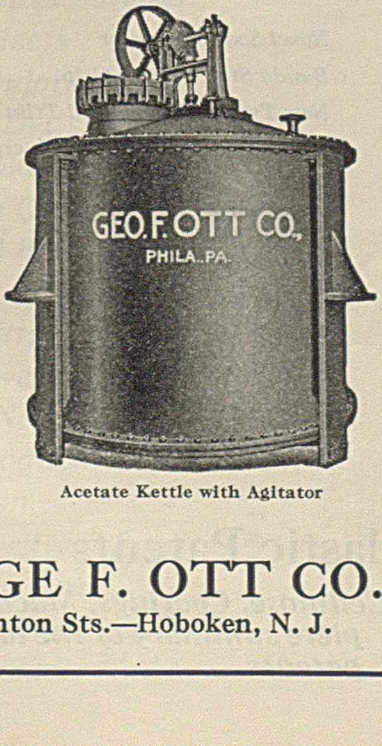
Established 1872
Engineers and Manufacturers
415-432 S. Clinton St. Chicago, Ill.

OTT SINCE 1870

Copper Equipment for All Industries

We make a specialty of building apparatus to suit your particular needs. Among our products are:

- Stills
- Evaporators
- Autoclaves
- Heaters
- Jacketed
- Kettles
- Digesters
- Tanks
- Coils
- Pipes and Fittings



Acetate Kettle with Agitator

GEORGE F. OTT CO.

8th & Clinton Sts.—Hoboken, N. J.

HILLS-McCANNA

(SAUNDERS PATENT)

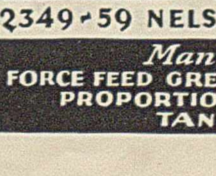
VALVE

OFFERS THESE ADVANTAGES:

WORKING parts never in contact with materials handled.

Liquid areas lined with Glass, Rubber or Lead, or made of Corrosion resisting materials, such as, Alloy Steel, Non-ferrous Alloys, Ceramics and Synthetic Resins.

No machine shop maintenance to keep valve in service. A wrench and oil can are the only maintenance tools needed.



Prices and literature upon request. Please name liquids to be handled, pressures and temperature.

HILLS-McCANNA Co.

2349-59 NELSON ST. *Chicago*

Manufacturers of
FORCE FEED GREASING AND OILING SYSTEMS
PROPORTIONING PUMPS, ALLOYS
TANK CAR VALVES

How the February issue of Plastic

Editorial

The NRA Whirligig

We have had seventeen letters, two telephone calls, and a post-card commending this editorial—have you read it?

Feature Articles

Premiums From the Plastics Point of View

Do you know just where premiums stand under the NRA, and can you guess how many million pounds of molding powder is going into this trade in 1934? Nathaniel Williamson tells you both, and more too, in this article.

Measuring Plasticity of Hot Molding Compounds—The Flow Tester

Since the war, Bakelite has been experimenting to perfect a machine for measuring plasticity. Gilbert L. Peakes describes the design and construction of the Flow Tester they have just developed. The next two issues continue this story, with instructions to operate the machine and comparisons of a great many tests already made.

Applications of "Acetate," a review of typical uses of this molding material

Spencer Palmer, who of all men ought to know, summarizes in detail both the product and the manufacturing advantages of cellulose acetate, and gives a complete table of its physical characteristics.

Chemical Tests for Transparent Papers

All that glitters is not cellophane, and here are detailed tests for distinguishing between the various transparent, plastic papers, according to the source of the raw material.

Industrial Coatings

How to Sell Color

Packard "stole the show" at both New York and Chicago with a display deliberately designed to sell color. How they did it and why is told in an interview with Herbert Thompson Strong, the colorist-in-charge, and it is full of practical hints for anyone whose goods have any color appeal whatsoever.

Turpentines—Artificial, Synthetic and Substituted Types. Reviewed and described by Ibert Mellan

Ibert Mellan reviews the artificial, the synthetic, and the substituted types of these important solvents, with a good check-list of the basic patents involved.

Summary of

Helpful Hints

Plastic Molding—a book review

Lacquers and Varnishes for Railway

Cellophane for Determining Humidity

Titanium in Paper—and in Plastics

Insoluble Coatings for Air Drying Resin Varnishes

Plastics in Pictures

Seventeen pictures in Sepia Ink on India tint paper, that show more new and novel applications of plastics and coatings than we usually have been able to collect in this department, which is one of the most popular, regular features of PLASTIC PRODUCTS—a style-sheet and news-sheet that you certainly will enjoy and find exceedingly profitable.

Novel Soap Dispenser
Banda Stair Carpet Grip
New Type of Metal Wall Trim
Jars—ideal for delicate face creams
Rotary Knife Sharpener
Bridge Ash Tray
New Telephone Index
Display Light
Spot-O-Lite
Lapel Microphone
A new tree wire guard
Plastic closures

Plastic Patents

Cellulose, Coatings, Machinery: a complete summary of the last 30 days U. S. patents.

Products

keeps its readers up-to-date

the Contents

News of Plastics and Coatings

Packaging Clinic
NRA and Packaging Problems
"Clinic" Plans
Premium Exposition
Newark, N. J. shows Plastics
Alliance Exhibit Plans
Exhibit of "Man-Made Materials"
Williams, NRA, resigns
DuPont Viscoloid Suit Winner
Chicago Furniture Style Show
Elton Succeeds McFadden
Glidden Acquires Patents
A.S.T.M. Projects
Coatings Standards
Committee "D-1's" Program
Fabricators' Code Submitted
Liquor Bottle Caps
Novel Molded Base
New Recruits to Molded Tops
Important Litigation
Cellulose Survey
Safety Glass News
Sylvania Introduces
In Washington
Interesting Delivery Service
Personal—Personnel
From Foreign Plastics News
Company Booklets

IF you are interested in plastics do not fail to watch the pages of the only magazine in America devoted wholly to synthetic resins, molding powders and molded products, coated and impregnated fabrics, lacquers, synthetic coatings, etc. Nine out of ten chemists agree that the great chemical development of the next ten years is going to be in the plastics field—"it pays to be posted"—no other journal can give you the up-to-the-minute information that you will find in every issue of PLASTIC PRODUCTS.

USE THIS COUPON TODAY

Plastic Products
25 Spruce Street, New York City

Of course I am interested in plastics. Enter my subscription for 12 months, and bill me for $3.00.

Name..

Address..

Position..

PROFESSIONAL DIRECTORY

Personal Services Only

1-Inch Card, $4.40 per Insertion. ◇ 2-Inch Card, $8.80 per Insertion.

DR. HENRY ARNSTEIN
191 E. Roosevelt Boulevard
Philadelphia, Pa.

Expert in Fermentation and Distillation

Specializing in the construction and operation of

Breweries, Sugar Factories, Distilleries, Alcoholic Motor Fuel Plants

and in the recovery of

By-Products (Yeast, Liquid & Solid CO_2 Cattle-Feed, Corn Oil etc.)

Complete Chemical and Food Producing Plants Constructed and Operated

---

BENJAMIN T. BROOKS
Chemical Engineering and Development
Since 1912
114 East 32nd Street
New York, N. Y.

GUSTAVUS J. ESSELEN, INC.
Chemical Research and Development

An Organization Experienced in the Application of Chemistry and Chemical Engineering to Industry and Business.

Cellulose and its derivatives
Textile fibres and fabrics
Dyes and their applications
Pulp Paper Leather Rubber
Industrial Bacteriology Synthetic Resins

73 Newbury Street Boston, Mass.

F. B. Porter R. H. Fash
B.S. Ch.E., Pres. B.S., Vice-Pres.
THE FORT WORTH LABORATORIES
Consulting, Analytical Chemists and Chemical Engineers

When you have propositions in the Southwest consider using our staff and equipment to save time and money.

Fort Worth, Amarillo, Dallas, Houston and San Antonio

FOSTER & CODIER

Specialists in Chemical and Metallurigical Patents and Applications Involving Processes and Products.

Ex-Examiners in Chemical Divisions,
U. S. Patent Office

726 9th St.
Washington, D. C.

FROEHLING & ROBERTSON, INC.
Established 1881

Inspection Engineers and Chemists

Richmond, Va. New York, N. Y.

OREGON B. HELFRICH
Jenkintown, Pa.

CHEMIST
Expert Knowledge of Lacquer Solvents and Plasticizers

Dr. Walter Cross Dr. Roy Cross
KANSAS CITY TESTING LABORATORY
Chemists—Engineers—Inspectors
700 Baltimore Ave., Kansas City, Mo.

LABORATORY OF VITAMIN TECHNOLOGY
Vitamin Assays of Food Products and Pharmaceuticals
Howard J. Cannon, Director,
1409 East 61st St. Chicago

MEIGS, BASSETT & SLAUGHTER
Incorporated
"From Research to Plant in Operation"
Chemical Engineers
Research—Design—Engineering
Reports on Projects for Financing
Drexel Building Philadelphia

ROBERT E. SADTLER
Attorney at Law (Tenn.)

Registered Patent Attorney
Chemical and Metallurgical Patents

Hibiscus Park Gainesville, Fla.

Established 1891

SAMUEL P. SADTLER & SON, INC.

Consulting and Analytical Chemists
Chemical Engineers

Special and Umpire Analyses
Small and Large Research Projects
Legal Testimony and Patents

210 S. 13th St., Philadelphia, Pa.

"Nothing Pays Like Research"

Harvey A. Seil, Ph.D. Earl B. Putt, B.Sc.
SEIL, PUTT & RUSBY
Incorporated
Consulting Chemists
Specialists in the analysis of
Foods, Drugs and Organic Products
16 E. 34th Street, New York, N. Y.
Telephone—Ashland 4343–4344

SKINNER & SHERMAN, Inc.

Research Analyses Physical Tests
Engineering Bacteriology

246 Stuart St. Boston, Mass.

FOSTER D. SNELL, INC.
Chemists—Engineers

A technical organization offering complete consulting research operating and management service.

305 Washington St. Brooklyn, N. Y.

IVAN P. TASHOF
Attorney and Counselor at Law
Patents

Specialist in the Protection of Inventions Relating to the Chemical and Metallurgical Industries

Victor Bldg., Washington, D. C

EDWARD THOMAS
Attorney-At-Law
Registered Patent Attorney

Chemical Patent Problems

Woolworth Bldg., New York City

THOMAS & HOCHWALT LABORATORIES
Incorporated

An organization offering complete chemical research and chemical engineering service. Pilot Plant facilities. Patents investigated.

Nicholas Road Dayton, Ohio

THE WESTPORT MILL
Westport, Conn.

Laboratories and Testing Plant of
THE DORR COMPANY

Chemical, Industrial and Metallurgical Engineers

JOHN PRICE WETHERILL
2819 McGill Terrace
Washington, D. C.

Chemical and Metallurgical Laboratory Research.
Patents consultation solicited.
Abstracts of Domestic and Foreign Patents and Translations of German, French, Italian, Polish, Czecho-Slovak Literature.

A. W. WILLIAMS INSPECTION COMPANY
Specializing in the inspection of
POLES, PILING, CROSSARMS, CROSS TIES, CONDUIT, LUMBER, STRUCTURAL TIMBER and PRESERVATIVE TREATMENTS
Analysis of Wood Preservatives
MOBILE, ALABAMA
Inspectors for Assignments at All Plants

Laboratory Efficiency
***Speeds* Up Production**

How about your laboratory furniture? Is it modern? Does it take up too much room? Does it offer you all the newest time saving features? In short, is your laboratory efficient?

Industrial Laboratory Table No. H-1543

STEEL OR WOOD FURNITURE

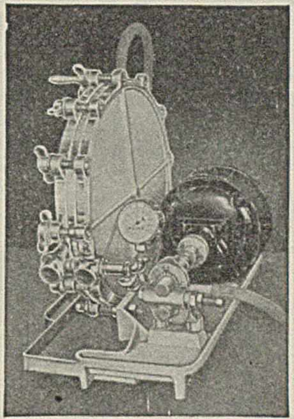
Right now is the time to get your laboratory in its best working order, for just ahead there is much work to be done. Perhaps you need steel furniture or specially designed furniture. Maybe all that is required is an extra table, desk or fume hood.

Regardless of your needs Kewaunee can supply them at reasonable prices. Write for a Kewaunee Engineer to call or ask for our big Kewaunee Laboratory Furniture Catalog.

Kewaunee Mfg. Co.
LABORATORY FURNITURE EXPERTS

C. G. Campbell, Pres. and Gen. Mgr.
110 Lincoln St., Kewaunee, Wis.
Eastern Branch: 220 East 42nd St., New York, N. Y.
Mid-West Office: 1614 Monroe St., Evanston, Ill.
Offices in Principal Cities

ULTRA-FINE FILTRATION
Means More Sales For You



HY-SPEED Type 102 Bench Model Electric Filter

Run your present filtered product through the HY-SPEED disc filters;—you will be astounded at the brilliance and sales appeal that these filters add to your product. These filters are, by far, the most advanced ultra-fine filters ever developed by engineers. The speed and excellence of their work will boost your sales considerably and cut your overhead. Hundreds of liquid processers have told us that.

HY-SPEED disc filters come with from 2 to 100 discs; will polish 1 to 50 or more gallons of liquid per minute. There is no installation cost; no labor.

We'll prove these facts. Ask for a 10 day free trial. There's no obligation, you know.

Write for a Free Catalogue

ALSOP ENGINEERING CORP.
39 W. 60th Street New York City
M'f'rs of disc filters, mixers, bottle fillers, glass coated tanks, etc.

The Catalytic Oxidation of
ORGANIC COMPOUNDS
in the Vapor Phase
L. F. Marek and Dorothy A. Hahn

This book is of interest to industrial chemists, petroleum technologists, workers in the field of the internal combustion engine, organic chemists, research workers and technologists in the field of oxidation reactions and those interested in the general field of catalysis.

It deals with catalytic, vapor phase oxidation which has long been used in the oxidation of methanol. The vapor phase oxidation of aromatic hydrocarbons has made available cheap phthalic anhydride, synthetic anthraquinone, cheap maleic, malic, and succinic acids, chloride free benzaldehyde and benzoic acid, etc. From petroleum oils oxidation is furnishing new chemical materials. Now, oxidation is being looked to as a means for the economic utilization of cheap gaseous paraffin hydrocarbons.

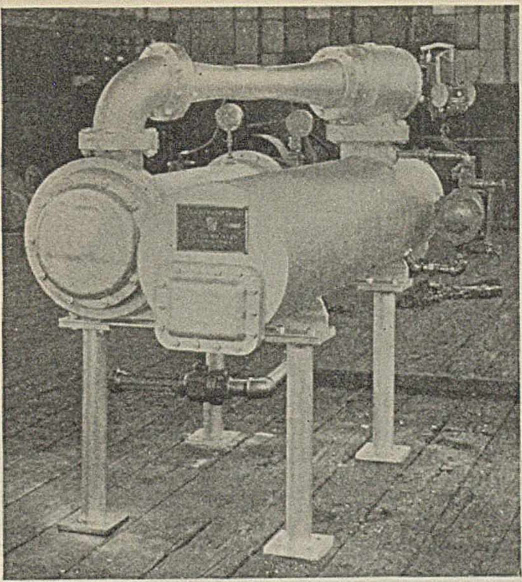
CONTENTS

Introduction—Catalysis
Catalytic Decomposition of Alcohols
Oxidation of Alcohols to Aldehydes and Acids
Reactions Involved in the Synthesis of Hydrocarbons and Alcohols from Water Gas
Oxidation of Methanol to Formaldehyde
Oxidation of Gaseous Paraffin Hydrocarbons
Oxidation and Hydration of Olefins and Acetylene
Oxidation of Petroleum Oils
Production of Hydrogen from Methane
Surface Combustion
The Cause and Suppression of Knocking in Internal Combustion Engines
The Oxidation of Benzene and Its Derivatives
The Oxidation of Naphthalene
The Oxidation of Anthracene and Miscellaneous Polynuclear Compound
Apparatus

A. C. S. Monograph No. 61 486 Pages Illustrated $9.00

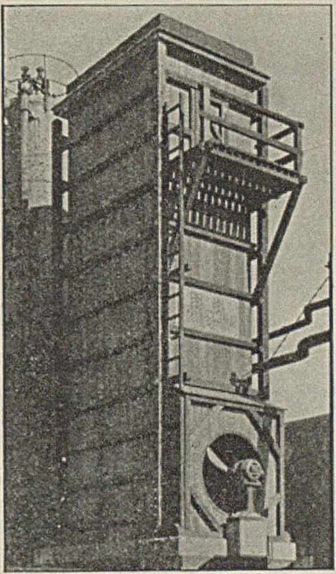
THE CHEMICAL CATALOG COMPANY, INC.
330 West 42nd Street New York, U. S. A.

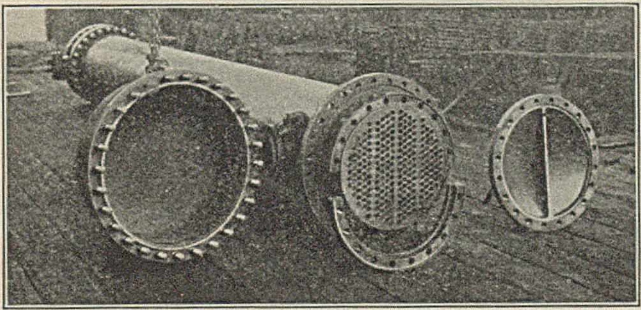
ALPHABETICAL LIST OF ADVERTISERS



Above: Ten ton vacuum refrigerating unit for the direct cooling of water. Since service water is used in the condenser the system has no moving parts.

Below: Forced draft cooling tower installed by Foster Wheeler for the North Shore Coke and Chemical Company. This is a single cell tower equipped with an aeroplane propeller type fan mounted on the shaft of its drive motor.





Left: Liquid to liquid heat exchanger showing the split ring developed by Foster Wheeler to make a compact floating head assembly. The tube bundle can be removed even though there is but slight clearance between the shell and tubes.

Coolers

For Water and Other Fluids

No industrial or chemical cooling problem is too unusual to be handled by one or more of the large variety of Foster Wheeler coolers.

Cooling towers for industrial or power water are offered in all designs, including forced draft, induced draft, natural draft and atmospheric types. These towers are made of wood or various fireproof materials according to individual requirements.

Vacuum refrigeration systems are used for direct and indirect cooling of many liquids and for direct cooling of water to temperatures below the range of cooling towers.

Surface coolers include many types for every conceivable problem involving gases and liquids. Frequently used types include, plate, shell and tube, double pipe and atmospheric coolers.

Foster Wheeler Corporation, 165 Broadway, New York.

FOSTER

WHEELER