INDUSTRIAL
EDITION
VOL. 25, No. 1

January, 1933

Industrial AND ENGINEERING Chemistry

VOL. 25, CONSECUTIVE NO. 1

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:
419 Fourth Ave.,
New York, N. Y.
TELEPHONE: Lexington 2-4186

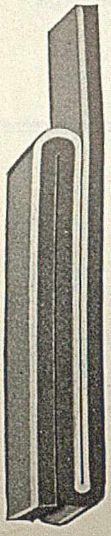
CONTENTS

20,700 Copies of This Issue Printed

Subscription to nonmembers, $7.50; single copy, 75 cents, to members, 60 cents. Foreign postage $1.50, except to countries accepting mail at American domestic rates and to Canada. 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 sixty 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.

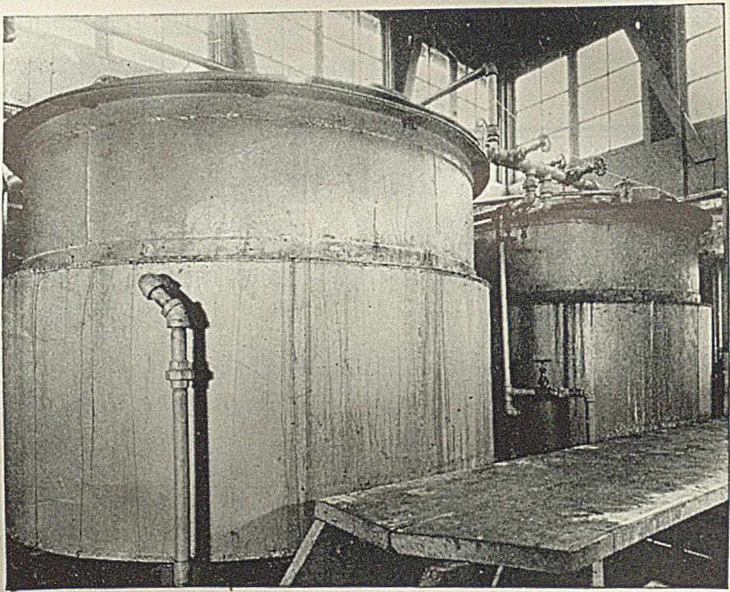
The AMERICAN CHEMICAL SOCIETY also publishes the *Journal of the American Chemical Society* and *Chemical Abstracts*.

STAINLESS STEEL SERVICE
now costs much less!



—A severe test demonstrating the permanent bond of the metals that form Ingersoll Stainless Clad Steels.

Ingersoll Stainless-Clad Steel makes stainless steel service available in countless places where hitherto the price has been prohibitive. The Ingersoll Ingot Patented Process is one of the recent sensational developments in the steel industry. It combines the non-corroding and acid-resisting qualities of stainless steel, such as 18-8, with the economy of low carbon steel construction. Savings of approximately 50% in material costs are made possible.



—The above tanks were produced from Ingersoll Stainless-Clad Steel for a manufacturer at a very large saving over other acid-resisting tanks formerly used in this industry.

Investigate the Advantages offered you by
Ingersoll Stainless-Clad Steel

—Where you must have stainless steel, consider the savings Ingersoll Stainless-Clad Steel affords over the solid stainless metal.
—Where you would like to have stainless metal, but have gotten along without because the price was prohibitive, you can now afford Ingersoll Stainless-Clad Steel.

Ingersoll Stainless-Clad Steel is produced by an entirely new and superior process—"Welded in the Ingot." A finest quality 18-8 stainless ply of 10% or 20% for plates, and 20% for sheets, is perfectly and permanently bonded onto a base of low carbon steel. The two metals form a complete union which is not affected by manufacturing processes nor by subsequent use.

Ingersoll Stainless-Clad Steel may be formed, drawn, spun, beaded, braised, welded, soldered and fabricated, with practically the same equipment used in handling regular low carbon steels.

For VATS—TANKS—DRUMS—TABLE TOPS—KETTLES—VENTILATORS
SHAFTS—FUME HOODS—STACKS—ETC.

—it provides stainless steel service at much lower cost.

Investigate Ingersoll Stainless-Clad Steel and the importance of this discovery to industry, particularly wherever chemicals are used or produced. Our engineers are at your service.

INGERSOLL STEEL & DISC COMPANY
(A Division of Borg-Warner Corporation)
Specialists in high carbon, alloy and high speed steel sheets.
310 South Michigan Avenue, Chicago, Illinois
Plants: Chicago, Illinois and New Castle, Indiana

INGERSOLL Trade Mark Reg.
STAINLESS-Clad-STEELS
MADE BY THE INGERSOLL INGOT PATENTED PROCESS

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

Overheard about This Issue

Those Who Wish may weep for the passing of 1932. For our part, the dead past may bury it deep with no tears from us. At least its demise supplies the opportunity for hope, and, where hope is, there must be life and the power of doing. May we add our voice to those wishing you hope, opportunity, and accomplishment in 1933.

Air-Conditioning occupies our first attention in this issue—a pertinent subject when cold and snow and ice have robbed the atmosphere of its accustomed moisture and warmth. Hanley (page 9) discusses the value of properly controlled air in the essential industry of pharmaceuticals and shows how efficiency both of operations and workers can be increased by proper adjustment of moisture, temperature, and velocity of air in the manufacturing department. Williams (page 13) describes the installation of similar equipment in the confined spaces of railroad cars and the effect this has had on the comfort of travel. In both situations the expense of installation has been fully justified, according to these authors, on the basis of dollars returned.

Finishing Ferrous Surfaces has received so much attention on account of its relation to corrosion, that the equally important subject of finishes for other metals has been neglected. Here is a symposium presenting several different aspects of the subject of industrial significance, not only to those who would apply such finishes, but to the makers of paints, varnishes, and lacquers as well. Whitmore (page 19) deals at some length with the finishing of the light metals used in airplane construction. He points out what many are likely to overlook—that these must be protected with the utmost care from corrosion because of the pronounced effect it may have upon their properties. Edwards and Wray (page 23) confine themselves to aluminum surfaces and emphasize the importance of pretreatment of the surface to allow the applied film to adhere properly. Nelson and Kittelberger (page 27) discuss the application of finishes to zinc and zinc alloys. The first of these papers adopts the user's point of view, the two following, the metal manufacturer's, and so it is only fitting that the final paper present the views of a maker of finishes. Corbin (page 32) discusses the finishing of zinc from the point of view of the materials used.

Protection against Corrosion and erosion of the vast systems of pipe lines, carrying oil and gas about the country, is the subject of serious discussion by Gill (page 49). After considering the many available methods of protection, this author is inclined to conclude that the ideal has not yet been attained in this field, and that the annual losses, estimated as approaching 150 million dollars, make that solution well worth finding. The size of our pipe-line systems is rather staggering when one realizes that nearly half a million miles of lines made of some 30 million tons of steel are in service in the United States.

Washing with Sodium Metasilicate may, under some circumstances, result in the formation of gels which hold the dirt in milk bottles rather than remove it. Prucha and Getz (page 68) have studied the conditions under which gels form and are able to point out ways to avoid it and to utilize to the utmost the cleansing operation. Dairies and others having glassware to wash, as well as the compounders of detergent mixtures, will find much of value in this paper.

A Look Behind often helps to put current events into their proper perspective. Shepard (page 35) gives us a century-long view of the development of the rubber industry.

Selection of the Carbon used in water purification apparatus is essential according to Behrman and Gustafson (page 59) who have found that corrosion of such equipment proceeds rapidly when certain activated chars are used without proper provisions to prevent it.

Compounding Ingredients in rubber insulation seriously affect its electrical properties, and now Ingmanson, Scharf, and Taylor (page 83) point out that accelerators and antioxidants, usually present to a very slight extent in the final product, may also be the causes of high electrical losses.

Molds That Attack Lumber from our southern forests and degrade it by stains take serious toll from this industry in reduced value of its product. Lindgren, Scheffer, and Chapman (page 72) have given the matter exhaustive study, and report at length on results of tests with more than a hundred possible remedies for the trouble. They point out that perhaps five of the many materials tried are really effective at permissible costs under the conditions necessary for industrial practicability.

Oriental Folk Practices supply what Owen (page 87) suggests as a valuable method of reducing the cost of industrial alcohol produced from grain. It is true that the amylo process he advocates is now several generations removed from the manufacture of the beverages of the Chinese and Japanese through adoption and adaptation to the alcohol industries of Europe, but nevertheless the conversion of starches to fermentable sugars by the method suggested is different only in refinement and application from that practiced for uncounted generations in the Far East.

What Really Has Happened to us during the past three years? Individually we are all inclined to overestimate and overstate the changes in matters affecting us, and so it is not strange that our collective reactions should also contain a distinct element of exaggeration. Wilson (page 104) is able to give us the cold facts about our activities in the chemical and related groups of industries before and during the present depression. There is little real comfort in knowing now that it has not been as bad as we supposed, but there is hope in the knowledge that we have less far to climb out than our pessimism had led us to believe. That last is worth all the shock of learning that we haven't been as sick as we thought.

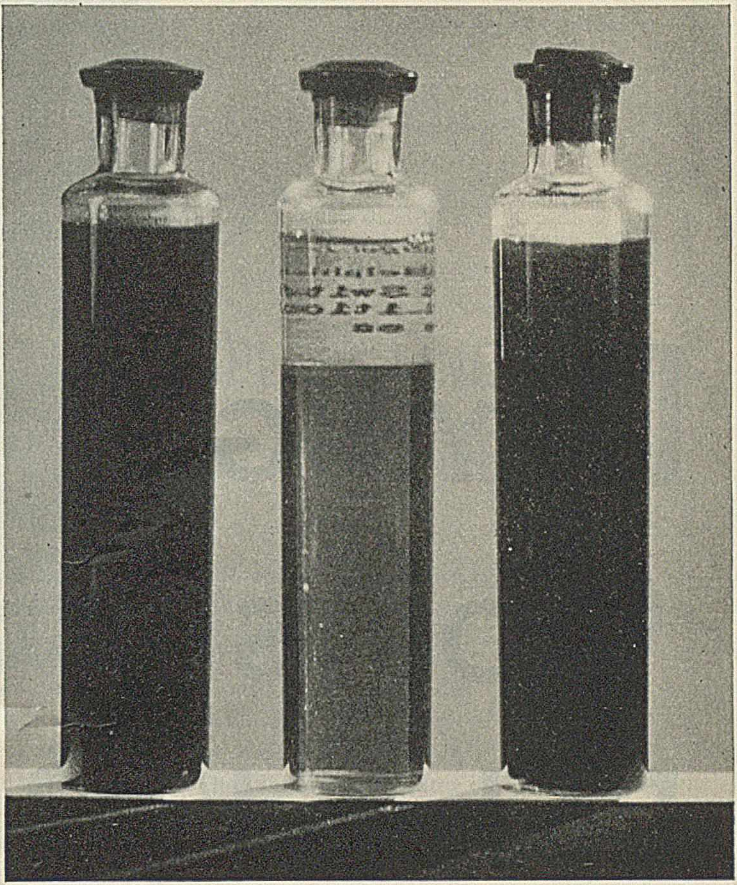
The Humanities are often neglected in the profession of chemistry, and so it is refreshing to find the Presidents of the American Chemical Society reviewed for us as men as well as chemists. Hale and Nelson (page 110) summarize the histories of those who have led the Society during its 56 years of history, and, even though the account smacks somewhat of the detached spirit of research, these leaders are shown to be—as most heroes are—very human after all.

Again, our best wishes for the New Year. May we hear much good of you during 1933.


USE NO HOOKS
200 Lbs.
PURE TRIPOLI FLOUR
SENECA STANDARD
BARNSDALL TRIPOLI CO.
SENECA, MO.
U.S.A.
"SUBSIDIARY BARNSDALL CORPORATION"
"SUBSIDIARY BARNSDALL CORPORATION"

WETTING OUT PROPERTY OF SILICATES

AN ANSWER TO MANY PROBLEMS



Reclaimed switch oil. Left hand: Used switch oil after ordinary centrifugal treatment. Dark and opaque. Center bottle: Used switch oil reconditioned with silicate of soda. Clear, amber color. Transparency indicated by printing on label on reverse side. Right hand: Oil from switch in service.

WHETHER it be the restoration of the lubricating value of the oil in your auto crank case, or the renewing of the freshness of your shirt, P.Q. Silicates possess that essential property for the removal of dirt—wetting power.

Silicate solutions have been extensively used in reclaiming and refining processes involving the removal of foreign matter from oils. The same phenomena come into play in cleansing operations such as the washing of clothes or the removal of oily materials and solid dirt from metals. The instances where the ability of silicates to wet has practical importance, are various, and we review a few outstanding ones.

RECLAIMING DIRTY DRY CLEANING SOLVENT

Metso Sodium Metasilicate permits of better wetting action than caustic, and saponifies fatty acids more efficiently. Metasilicate separates better from the immiscible medium in which it is suspended, thus clean solvent is obtained at higher rates of flow than would otherwise be possible.

RECLAIMING USED CRANK CASE OIL

"B-W" Brand or "O" Brand agitated with the oil is able to wet carbonaceous and other suspended solid impurities, so that when the oil is floated upon water the solids settle to the oil-water interface, and with the aid of the silicates, neatly cross from the oil into the water layer. The clarified oil is then drawn off.

REFINING VEGETABLE OILS

The use of "N" Brand Silicate with the caustic permits of a higher recovery of oil, free from excess free fatty acid and coloring materials.

If you have a problem of removing impurities or dirt, which has not been solved, or which you believe might be improved, consider P.Q. Silicate of Soda, of which there are 33 grades, varying in ratio from 1:1 to 1:4. Our research in silicates and their uses covers over three quarters of a century.

PHILADELPHIA QUARTZ COMPANY

General Offices and Laboratory
121 S. THIRD ST., PHILADELPHIA
Chicago Office: 205 W. Wacker Drive
Sold in Canada by National Silicates, Ltd., Brantford, Ontario

Reg. U. S. Pat. Off.

PRODUCT
Crushed rock of low moisture-content

OPERATING COST per TON

FORMER DRYER	
Labor, fuel, power	$.433
Repairs, replacements	.052
Depreciation, taxes	.020
Interest on investment	.012
TOTAL	$.517
LOUISVILLE DRYER	
Labor, fuel, power	$.263
Repairs, replacements	.012
Depreciation, taxes	.030
Interest on investment	.018
TOTAL	$.323
SAVING (per ton output)	$.194
ANNUAL SAVING of LOUISVILLE DRYER	$20,000.

DRYING COSTS Reduced $20,000.00

HERE is a not-unusual case where a Louisville Dryer engineer saved his client $20,000 per year *merely by specifying a dryer of the proper size.*

The former dryer was of exactly the right type. It was correctly designed and installed. Its capacity had simply been over-estimated—and the resulting overload was seriously impairing efficiency.

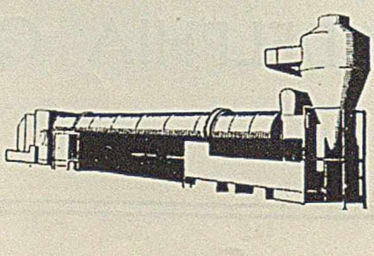
Things like that don't slip by Louisville Dryer men. Perhaps it's because we believe our job is to sell economical dryer *performance* rather than "the value added by manufacture" to our raw materials.

As a result, your consideration of Louisville Dryers is solicited only if it can be proven that they will produce more net profit to you than any other possible equipment.

* * *

If you are faced with the necessity of purchasing a new dryer—if you are interested in cutting present production costs, write for an outline of the Louisville Dryer plan. It explains how we analyze your drying conditions and submit definite cost-comparisons for your consideration. Incidentally, it shows how Louisville Dryers can frequently be paid for on "out-of-savings" arrangements. No obligation, of course. *Address:* Louisville Drying Machinery Co., *Incorporated,* 433 Baxter Ave., Louisville, Ky.

LOUISVILLE DRYERS



THE NAME

Taylor

NOW IDENTIFIES OUR COMPLETE LINE OF PRODUCTS, INCLUDING *Tycos* INSTRUMENTS

As of January 1, 1933, the Taylor Instrument Companies will generally replace the name Tycos with that of Taylor.

After that date, new types and designs of Taylor Instruments as well as containers, descriptive material and advertising will carry the name Taylor. Tycos-marked instruments, with a few exceptions, and Tycos material produced prior to that date, for sale during the year 1933, will carry our label stating, "The Name Taylor Now Identifies Our Complete Line of Products, Including Tycos Instruments," until their inventory is exhausted.

We consider it advisable to use one general trade name in place of two in the future to avoid any misconception about the uniform quality of Taylor products. This is a change long anticipated as a result of the continued growth of the Taylor Instrument Companies. It must be immediate in view of our plans to bring out new items and to start the most extensive advertising promotion ever undertaken by the Taylor Instrument Companies.

A recent survey of the United States convinced us that the name Taylor, placed on our products for homes, trade, professions and industries, will best represent the high standard of quality and accuracy established by the Taylor Instrument Companies through more than eighty years of business life.

President

Taylor Instrument Companies
ROCHESTER, NEW YORK

Taylor INDICATING, RECORDING AND CONTROLLING INSTRUMENTS

In a Crisis Would You Call A Patent Medicine Vendor or a Skilled Physician ?

THE answer is obvious. One provides standard remedies for every human ailment. The other carefully diagnoses **each individual case,** makes such tests and observations as are necessary, and, backed by a wealth of experience and specialized knowledge, recommends and applies the proper corrective measures.

■ These are times when necessary plant changes, replacements, enlargements or improvements can create a situation which has many of the aspects of a real crisis. Decisions must be made which deserve the help of trained specialists whose knowledge and experience **goes beyond the immediate items** under consideration. Continued health and satisfactory growth of any business can be seriously affected by factors which, on their face, seem to have little direct connection with a purchase being made. But these factors, **intelligently valuated** by one who recognizes their relation to your entire operating flow-sheet, may suggest things which would otherwise be overlooked. The "take-a-chance" decisions of those busy, large-profit days of a few years back when there wasn't always time to give a question proper study (it might have been logical then to use the remedy most available and convenient) are hardly excusable today.

■ We doubt if purchase decisions for major process machinery items should rest so largely on certain standard specifications. These specifications are no doubt necessary, but isn't it more important to do business with an organization which combines broad experience with a real knowledge of process work; one that can diagnose a problem and conduct research studies where necessary; and recommend, build and put in service equipment that **dovetails perfectly into the plant as a whole?**

■ Leader offers that type of organization. Ours is more than a modern, efficient shop where standard jobs are fabricated. We build into every unit of process machinery those factors which make our equipment **harmonize** with your entire economic set-up. We have more to sell than blueprints and metal and shop labor. Why not give us a call the next time anything of this sort comes up? Many old friends and new ones are discovering that they receive much more than a contract specifies when they do business with us—and these intangibles, these harmonizing features, can be of great importance in the results obtainable from any unit process.

LEADER INDUSTRIES, INC.

DECATUR, ILLINOIS, U. S. A.

RESEARCH — ENGINEERING — MANUFACTURING — CONSTRUCTION — FINANCE — OPERATION

Leader offers the following:

- DISTILLATION EQUIPMENT
  - Fractionation Units
  - Stills — Towers
- HEAT EXCHANGERS
  - Heaters — Coolers — Condensers
- EVAPORATORS
  - Single and multiple effect
  - Vacuum and Pressure Type
  - Natural — Accelerated Circulation
- DRYERS
  - Rotary and Chamber Types
  - Direct Fired — Steam Heated
- CRYSTALLIZERS — Jacketed Vessels
  - Rotary Kilns — Fumigators
- RUBBER LINED and Lead Lined Apparatus
  - Pressure Vessels — Any size any pressure

Complete plants also supplied where the major operations are conducted in these units of process machinery

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

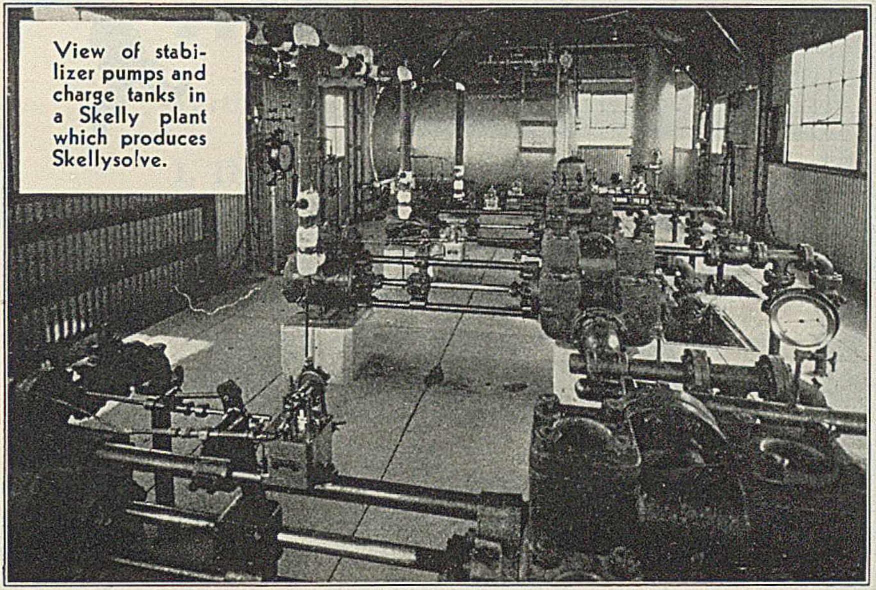
Xylidine

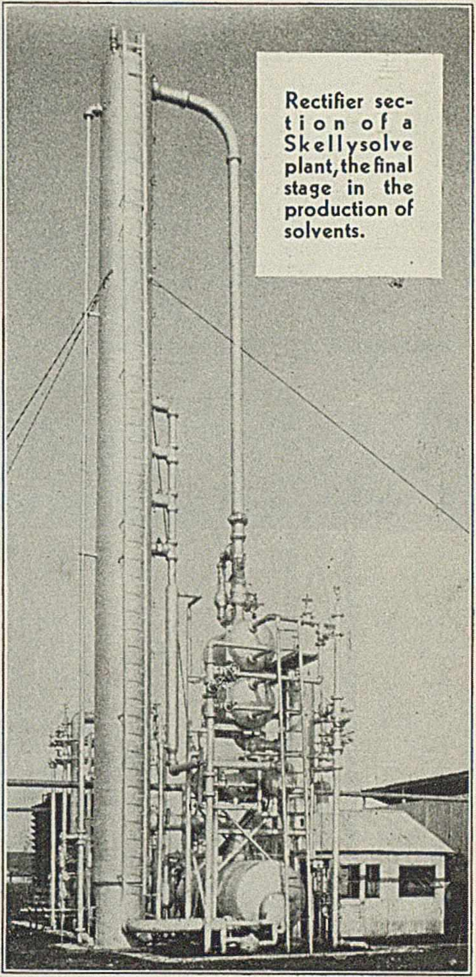
NATIONAL ANILINE & CHEMICAL COMPANY, INC.
(Intermediates Division)
40 Rector Street
(Bowling Green 9-2240)
New York City

NATIONAL N DYES

INTERMEDIATES

IN THIS PLANT


View of stabilizer pumps and charge tanks in a Skelly plant which produces Skellysolve.


Rectifier section of a Skellysolve plant, the final stage in the production of solvents.

WE MAKE SKELLYSOLVE FOR A WIDE VARIETY OF INDUSTRIES

Skelly Oil Company's program of specialization in producing solvents has included large expenditures in plants, equipment, laboratories and the training of men. The successful result of this pioneering has been the production of solvents that are constant in uniformity and exceptionally pure. In fact, Skellysolve has made available solvents with a quality beyond all previous experience in the petroleum industry; accordingly, these special fractions deserve your most careful consideration.

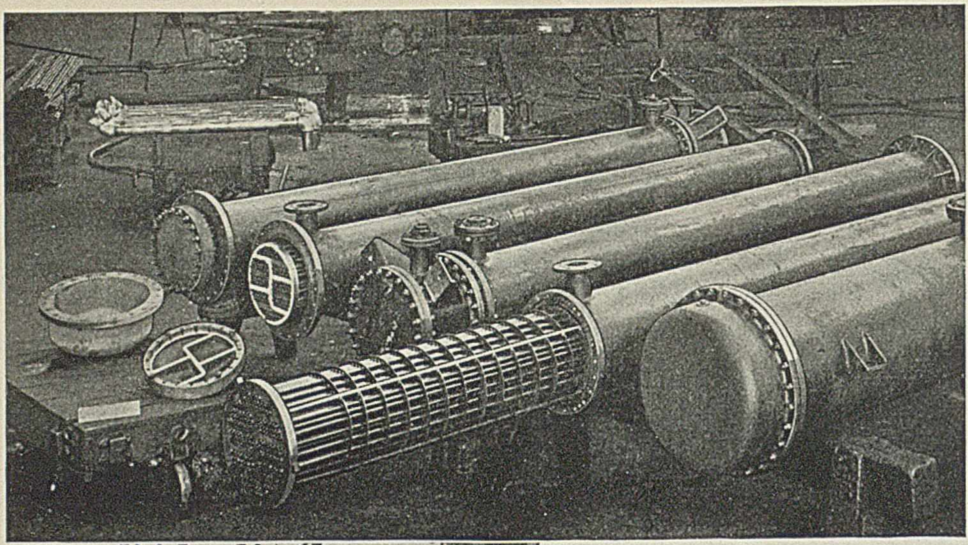
We are producing these special hydrocarbon fractions in a variety of boiling ranges, gravities and evaporation rates—for a wide range of laboratory and plant scale uses. We are the largest supplier of solvents to many types of industries because of the uniformity and consistently high quality of Skellysolve and because of our large production and transportation facilities.

These users—large and small—are effecting substantial savings through increased efficiency since using Skellysolve.

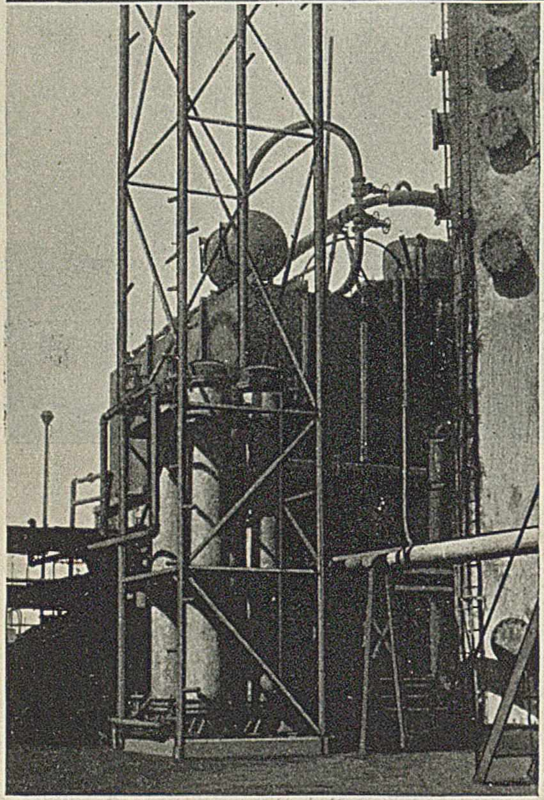
You, too, are interested in economy as well as using a better solvent. Then let us send you a generous testing sample to meet your specifications. Skellysolve is available in 10- and 55-gallon drums and tank cars. Today—write, wire or phone and ask for further information.

SOLVENTS DIVISION-SKELLY OIL COMPANY

121 WEST WACKER DRIVE CHICAGO, ILLINOIS




Vogt
FOR BETTER HEAT EXCHANGERS



A SELF-CLEANING CENTRIFUGAL

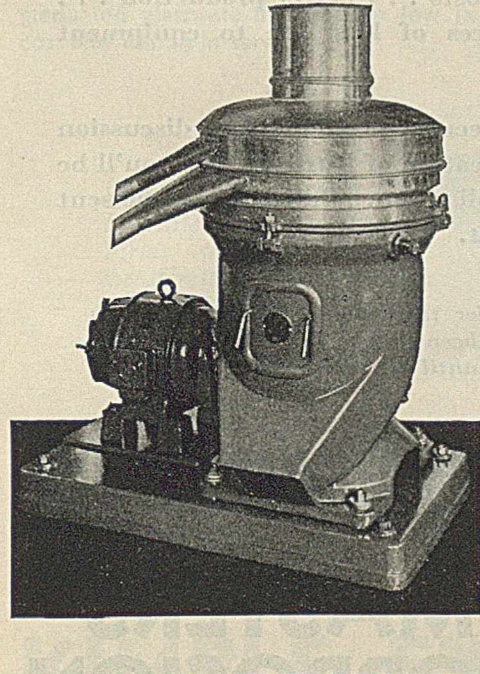
Giving Continuous Operation on Liquids Containing High Percentages of Solid Material

SHARPLES ROTOJECTOR

Particularly Adapted to —

1. The clarification of liquids containing high percentages (up to 10%) of amorphous and slurry percipitates.
2. The clarification of liquids where the labor cost of bowl cleaning would be high regardless of the equipment now used.
3. The separation of liquids which contain large amounts of solids (up to 10% by volume).
4. The reclaiming of valuable liquids held in slurries.
5. The recovery of valuable sludges without the labor of bowl cleaning.

The Rotojector periodically discharges its bowl cake in 10 seconds while running at full speed. It eliminates bowl cleaning labor, effects great savings over present filtering and settling methods and opens up new possibilities of economy and efficiency.



Write for our detailed report on the Rotojector

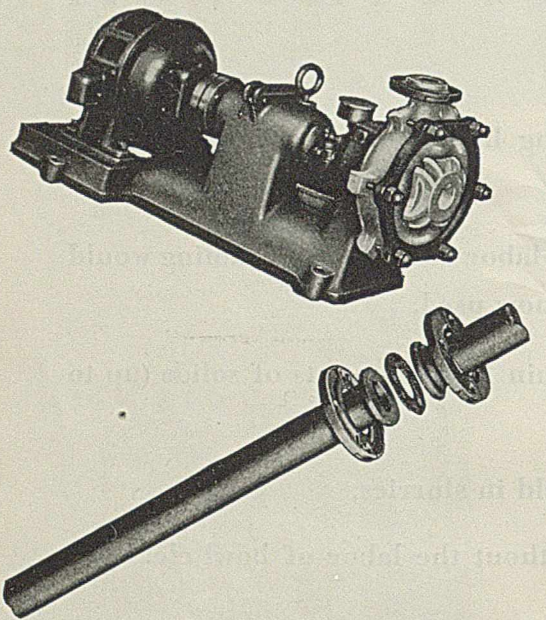
We will gladly test any samples in a full-sized Rotojector in our laboratories and give you a chemist's report advising what results you can expect from the machine. There is no cost or obligation.

SHARPLES

"FOR EVERY APPLICATION"

THE SHARPLES SPECIALTY CO.
2318 Westmoreland Street
Philadelphia, Pa.

Are you feeding Corrosion and charging the bill to "Maintenance"?



Some plants are doing just that needlessly, and, of course, the bill is included in their final costs of production.

Any reduction in plant maintenance costs—repairs and replacements—enables any plant to meet competitive prices to better advantage.

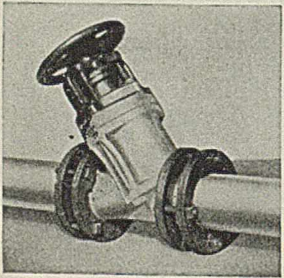
Consider how Duriron can be of help to you in reducing these costs. Duriron is solidly resistant to most corrosives. It is extremely hard and is not worn nor scoured by abrasives carried in suspension nor by high velocities.

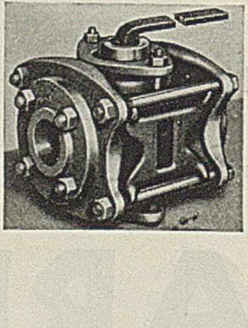
Duriron is made up into a multiplicity of forms such as pumps, valves, pipe and fittings, circulating steam jets, kettles, tanks, fans and other equipment. Special pieces of equipment are made to customer's order.

Take just a few moments and check over your corrosion losses and replacements due to corrosion. If Duriron can be used, you'll profit materially by it—improved product . . . lower costs . . . better production . . . fewer chances of loss due to equipment failure.

Our engineers are available for a discussion of the application of Duriron, and you'll be under no obligation. Bulletins will be sent upon request.

And consider this: Equipment from which parts have been "robbed" can't be put into production until the parts have been replaced.





THE DURIRON COMPANY, INC.
422 No. Findlay Street Dayton, Ohio

DURIRON MASTERS CORROSION

AMERICA'S FINEST K EXAX SCIENTIFIC GLASSWARE

One of the outstanding developments in the field of scientific glassware is the new EXAX BLUE LINE by Kimble. A real achievement---a marked departure---in the fabrication of fine glass laboratory apparatus.

Every graduation line and numeral on this clear crystal glass is filled in with a new BLUE glass enamel, actually fused-in as an integral part of the glassware. This new BLUE Enamel---more durable than any material hitherto used to fill in graduation marks---is applied by exclusive Kimble Process. It contrasts strongly against the crystal glass, making this new graduated ware unusually easy to read and accurate in operation.

RETESTED AND RETEMPERED

Every piece of Kimble Glassware is retested and carefully inspected against error, blemishes and imperfections. Only perfect, flawless glassware reaches the consumer.

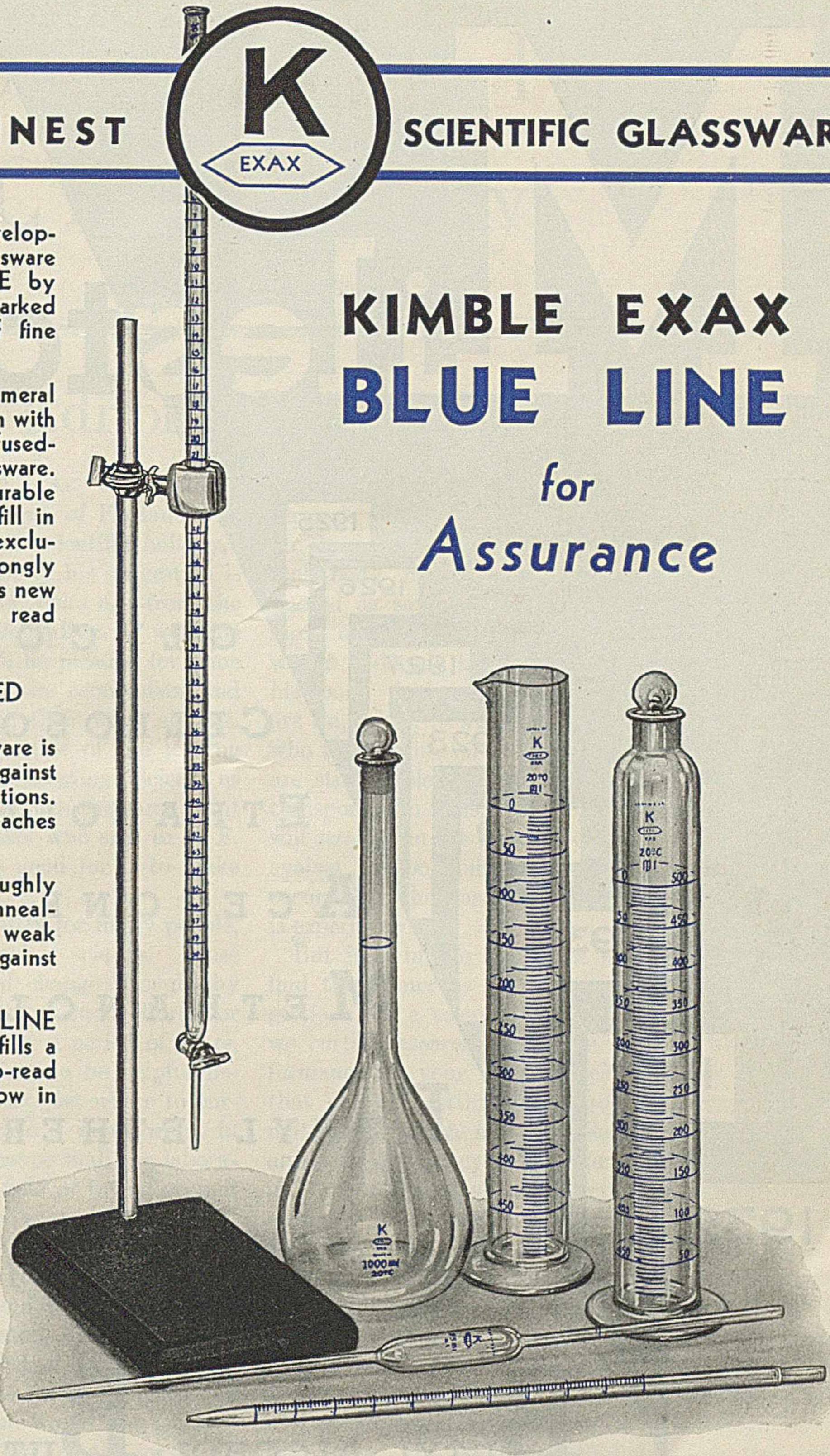
All Kimble Glassware is thoroughly retempered in a special lehr or annealing furnace, removing strains and weak spots, and protecting the ware against excessive breakage.

The new Kimble Exax BLUE LINE is complete in every detail. It fills a long-felt need for accurate, easy-to-read graduated glassware that is both low in cost and lasting in service.

◆ ◆ ◆

Stocked by leading Laboratory Supply Firms throughout the United States and Canada.

KIMBLE EXAX
BLUE LINE
for
Assurance



KIMBLE GLASS COMPANY, VINELAND, N. J.
New York, Philadelphia, Boston, Chicago, Detroit

KIMBLE EXAX BLUE LINE GLASSWARE

Industrial
AND ENGINEERING
Chemistry

Volume 25
Number 1

January
1933

Harrison E. Howe, Editor

The Editor's Point of View

SCIENCE MORATORIUM. As we recall it, it was a bishop of the Church of England who first demanded a "ten-year scientific holiday," but since then an occasional echo of his suggestion is heard. One of these came a few years ago from the lips of a college president in an address of welcome to a group of scientists, in which he pleaded for some opportunity for the sociologists, the economists, and humanitarians generally to bring their work abreast. Much more recently a writer in one of the leading financial papers, writing under the heading "Science as a Peril," again calls attention to much the same point of view as expressed by the banker who said to C. F. Kettering, "All that research is good for is to make banking hazardous."

Science has moved far too swiftly for many people, but that can scarcely be laid against science. Those who complain of the rapidity of change wrought by research and suggest a cessation of such efforts, or at least a temporary suspension for a period of years, uniformly fall short in their effort to be helpful because they do not tell the scientist just where to curtail his work. If we are to have a moratorium in science, along what lines of endeavor shall the laboratories be closed? And in what field of invention and discovery shall the experiments be stopped?

Of course there must be no diminution of effort where health and disease are concerned. We even support unnumbered researches and experiments which seem to have no possible application, in the hope that the minutest bits of truth established may have some bearing upon prolonging the useful and productive period of human life. Surely we would not ask the organic chemist to quit his search for the synthetic compounds required in specific cases to alleviate human suffering. Nor would we ask the scientist devoted to sanitation to forget for a time questions of public health and the safety of community life. Will anyone contend that we have yet found the ideal method of sewage disposal, or the best way of caring for city refuse? Perhaps science should pay no attention to the production of food, of which at the moment there appears to be an oversupply from the farmer's point of view, coupled with a woeful inability on the part of millions to acquire sufficient for normal body maintenance. Ornithologists have been quoted as saying that, should some catastrophe remove all the birds, the insects would overcome man within a decade by the simple process of destroying his food. So long as our insecticides and fungicides are imperfect, it would be a courageous man, indeed, who would cause efforts in these fields to cease. There are still problems of food storage, preservation, and transportation which are baffling and when solved will strengthen the bulwark already erected by science against the possibility of food shortage, when, as has occurred in the past, even a brief period of lean years is experienced.

But it is in the industries where we are likely to find the numerous examples which lead to the suggestions for a science moratorium. But where shall we curtail research? Are you satisfied with the performance of your automobile? Do you really feel that you are getting satisfactory efficiency from the motor fuel which must be placed in the tank with annoying frequency? Has the last word been said in tire design and construction? Forward-looking engineers already have stressed the single item of excess weight per passenger carried which one finds in the modern motor car and demand improvements which, in turn, require still further research in the light alloys of great strength. There are many combustion engineers who will tell us that there is still a vast amount of work to be done in the age-old field of fuel utilization. Shall we stop investigation in this field? The public has probably forgotten that, in the course of construction, two great bridges in the country failed and had to be rebuilt at great expense. Surely so long as such things can happen, there is work to be done in metals, alloys, and design. Highways still have the faculty of going to pieces before the bonds issued to build them are paid, and notwithstanding the great strides made within the decade in protective coatings and in nonrusting metals, there are still rust and decay. Waterproofing, fireproofing, insulation against noise, offer much to be desired.

In fact, wherever the human element is involved, something satisfactory for present use may exist but seldom, if ever, perfection. Show us perfection and we will show you where research may be unnecessary. Where there is imperfection, to declare a moratorium in science would be taking an incalculable and wholly unjustifiable risk.

⁂

PRIORITY. We all like to be the first with a new idea. Some prefer to record it in a patent application; others like to publish at once, knowing that this protects them in the United States for two years during which time they alone can file patent claims. In still other cases priority is a matter of professional pride, carrying with it the honors that come to those who are the first to do things. However, priority is not the primary purpose which activates most research. It is better to be right and to present a finished piece of work than to rush into print.

From time to time the question of priority comes forward for discussion. Some of our European colleagues prefer their plan of committing to paper the views and theories or the results of research and depositing a sealed document in some recognized place. At a later date this document may be recalled and, if the author likes, destroyed without anyone being the wiser or he may authorize the trustees of the sealed envelope to open it and publish the results to the world. The weak point in this plan is at once obvious. If later work proves the record made to have been in error, it is easily destroyed and no embarrassment is experienced. On the other hand, another working quite independently and arriving at the same conclusion may be confronted with the charge of old stuff by one who would rob him of the fruits of his labors by pointing to a prior work until that time unknown. This does not appeal to us as being just.

But what shall we do about priority, where it is important? We suggest that the received date stamped upon a manuscript in the office of any reputable scientific journal be regarded as the date upon which priority may be established. When a manuscript is offered for publication the author thereby declares to his scientific colleagues that his work has been carried to the point where it merits discussion and that he is prepared to demonstrate the validity of his claims. Possible delay in publication in no wise invalidates the received date. The presentation of a paper at a scientific meeting does not answer the same purpose. As any editor knows, there is often an interval of time between the presentation of the manuscript and when it is offered for publication. Suspicious ones would be the first to say that, in that interval, changes had been made in the manuscript. We offer, then, for universal adoption the suggestion made above that, where priority is concerned, the received date of the editorial office concerned be taken as the official date of disclosure.

⁂

ARCHITECTS. The slightest contact with the erection of any structure large enough to require the services of an architect will have demonstrated that, in common with most other classes of folk, there is a variety of kinds of these men who make the plans and in many cases determine the minutest details. Those who have specialized on a particular type of building and who are disposed to be coöperative are most helpful and, in fact, indispensable. There are others in whom the artistic temperament is so highly developed that they seem unable to view a building from any aspect other than its external impressiveness. If, perchance, one is concerned with a structure more or less monumental in character, which at the same time must be highly utilitarian, then indeed his architectural troubles begin. We recall an experience with a late architect who was outstanding from the point of view of new creations and who seems to have struck the only new note in the architecture of public buildings in decades. Those who found themselves unable to accept some of his suggestions were merely looked upon with pity by this man and no changes in plan resulted short of a miniature battle.

When it comes to the erection of chemical laboratories we have in addition to necessary utility a series of peculiar service requirements with which few architects are fully familiar. The note of joy and satisfaction is always apparent in the voice of the director who can say, "We had the full coöperation of our architect." And in such instances there is little, if anything, to criticize. How often we have heard, in explanation for some disappointment, "We just had to let the architect have his way, for he had the backing of the trustees."

Another phase of this problem is found in public buildings which are also laboratories. Here official procedure still further complicates the architectural relation. If the public is to be served adequately through the expenditure of its money and through the work subsequently done at minimum cost in the structure, the scientific staff must indeed gird itself for a number of major conflicts before the plans are completed and the specifications written. Let us turn, for example, to the new extensible building, two units of which have now been erected for the Department of Agriculture in Washington, with other units planned and under way. We are informed from an outside source that in the first of these buildings the most elemental details in laboratory construction were entirely overlooked, and those in charge of preparing and executing the plans were so obsessed with the need for hurry that at no time was it possible for the scientists who are to use these laboratories to make suggestions, direct changes, and submit suitable plans and layouts. Fans exhausting laboratory hoods discharged the fumes, not into the open air, but under the roof, requiring a very substantial expenditure, not only to put in the necessary vents but to replace metal work and other parts of the new structure which were soon so badly corroded as to make them unsafe. Last minute changes in the general idea for this extensible building resulted in the elimination of some cross-bridge and corridor construction, leaving a series of windows so narrow as permanently to decrease the utility of the rooms they serve.

Those who study the modern laboratory agree that vent flues, service lines, and the like should be carried along the corridors, making possible a flexibility in laboratory arrangements without which future usefulness of the building may be greatly hampered. In the best type of laboratory, partition walls are mere blocks of gypsum or other light construction that can be changed at any time with minimum expenditure. But not so where the architect proceeds unhampered. In the building under discussion where the flues are provided they are in the partition walls. One flue carries from the first floor to the roof, likewise the second and succeeding floors, with the result that in the upper floors most of the partition consists of flues and consequently can never be changed without virtually rebuilding the structure. Anyone interested in this case would also do well to inquire whether there is any ventilation provided other than that through the chemical hoods, and what provision, if any, has been made for the introduction of fresh air. When more than three hundred fans are at work exhausting air from various hoods, the question of satisfactory intake becomes serious. And where brought in it should be supplied from ducts in the corridors, so that the fresh air flow would be from the corridors into the laboratories rather than the reverse. Architects generally do not understand the service of laboratory vent flues and seem to overlook the need for acid- and moisture-resisting tiles, or some other resistant material laid up without the possibility of pockets for the accumulation of corrosive acids.

Not only the type of fan, but the way it is mounted and the size to insure free flow of air without too great velocity, which may cause vibration and noise, are important. Resistance and back pressure caused by bends must be considered, and the materials used for fan-housing must be chosen with respect to avoiding corrosion, repairs, and replacement. Likewise there must be proper drainage for condensation, rain, or snow.

Another mystery to our friends is that of suitable floor coverings where laboratory reagents are to be used. Some type of mastic floor of proper thickness and of standard quality laid in the form of tile or otherwise has proved advantageous. Linoleums do better for office floors. The distribution of water, gas, steam, compressed air, vacuum, and other services is a specialty, and for distilled water, block tin or aluminum pipe properly and adequately supported is essential. Waste lines of acid-proof materials are just as important and the finishing of walls with materials which will resist discoloration, adhere firmly in place, and reflect the maximum of light is required.

It is too late to rectify many of the errors and the damage done is really considerable, for it will mean increased expense in operation, maintenance, and early repairs, with a large outlay at some future time to make changes which cannot be predicted but which would be of no serious consequence had sufficient flexibility been provided at the outset. It is not too late to learn the lesson, however, and apply it to other parts of this extensible building yet to be erected. It should be remembered where laboratories are contemplated anywhere.

Let us pay attention to proper architecture. We must by all means have beauty, but a number of structures show this to be possible and still meet the peculiar requirements of the modern laboratory. We are confident architects will find no difficulty in working to the requirements of the scientist, but the plans must originate with the men who must use the building and these men must constitute themselves vigilantes until the very day of dedication.

⁂

THE FERMENTATION INDUSTRY. However you may contemplate the ultimate fulfilment of political promises that the fermentation industry is to be reëstablished, it is pertinent to point out that it cannot be tolerated without laws requiring the highest degree of excellence. Suitable standards cannot be set up without reference to reputable, recognized chemists and cannot be maintained without their continued supervision and watchfulness. In such discussion as has so far appeared this essential point has been omitted. A number of those who believe that the fermentation industries should be reëstablished are fearful lest the low standards of the criminal classes, in whose hands this industry now is, shall prevail, rather than those of a class of citizens with some sense of responsibility. At present, swinging from one extreme to the other in true American fashion, the trend appears toward abandonment of regulations, threatening to leave us without laws under which supervision could be exercised to control the chemical composition or suitability for beverage purposes of any products. If the industry is to assume anything like its predicted size, there will be required a great number of chemists properly to supervise production and to maintain the highest possible standards, without which nothing whatever will be gained and, indeed, the bootlegging industry will be practically legalized.

Those of us who are but academically interested in the subject but who remember the elaborate controls, the scientific laboratories, the institutes of brewing for the training of brew masters, the standards maintained by leaders in the industry, have been quite unable to understand how anyone could be so thirsty as to tolerate the hit and miss messes which have been dignified by the name of "home brew." If we are to have a fermentation industry again it should take advantage of every progressive step that has been made in materials of construction, in the design of equipment, in plant layout, in the selection and breeding of ferments, and all other phases of the science upon which it should rest. Fermentation research has not stood still in the last decade.

Put bluntly the question is: Is this potential two-billion-dollar industry, if, as, and when reëstablished, to be dominated by a class with bootleg standards, or by one such as is typified in the membership of the AMERICAN CHEMICAL SOCIETY? If you believe in high standards and their maintenance the time for you to express yourself is when legislation is being formulated, not after.

∴

SCIENCE AND THE SPOILS SYSTEM. So great a political turnover as was brought about by the last election seems certain to be followed by an extensive change in personnel in the various government bureaus. It is recognized that a considerable number of such appointees follow a given political banner and rise or fall with the success of their party. While this may be wasteful, in that experience is exchanged for inexperience, there are many activities which apparently suffer little by the exchange.

In the scientific bureaus of the Government, however, we meet a different situation. The scientist is a trained man. Even though appointed on a basis that might anticipate his removal with a change in party, he is chosen with regard to his training, his experience, and oftentimes a peculiar ability in a particular field of investigation which is quickly translated into service to the people at large. In many instances it would be most difficult to find his equivalent and even though another of equal promise might be secured, he obviously would lack the experience that had been gained through a number of years of special activity and concentration on peculiar problems. Science should not be subject to the spoils system. At all times those placed in the scientific bureaus of the Government should be chosen irrespective of politics and retained in office so long as ability, activity, service, and results justify.

∴

POST OFFICE REGULATIONS. The many among our readers who carefully observe all details of our publications will be quick to note new arrangements of mastheads and designations of volumes and numbers on the covers of our three editions. This change has been made to conform with the regulations of the Post Office Department, which require all editions of a publication to bear the same volume number and to have the issues consecutively designated. Therefore, on each edition, you will find reference to Volume 25 and a consecutive number. However, to avoid any confusion among libraries or those who use references to the three editions of INDUSTRIAL AND ENGINEERING CHEMISTRY, the special volume and number of each is indicated.

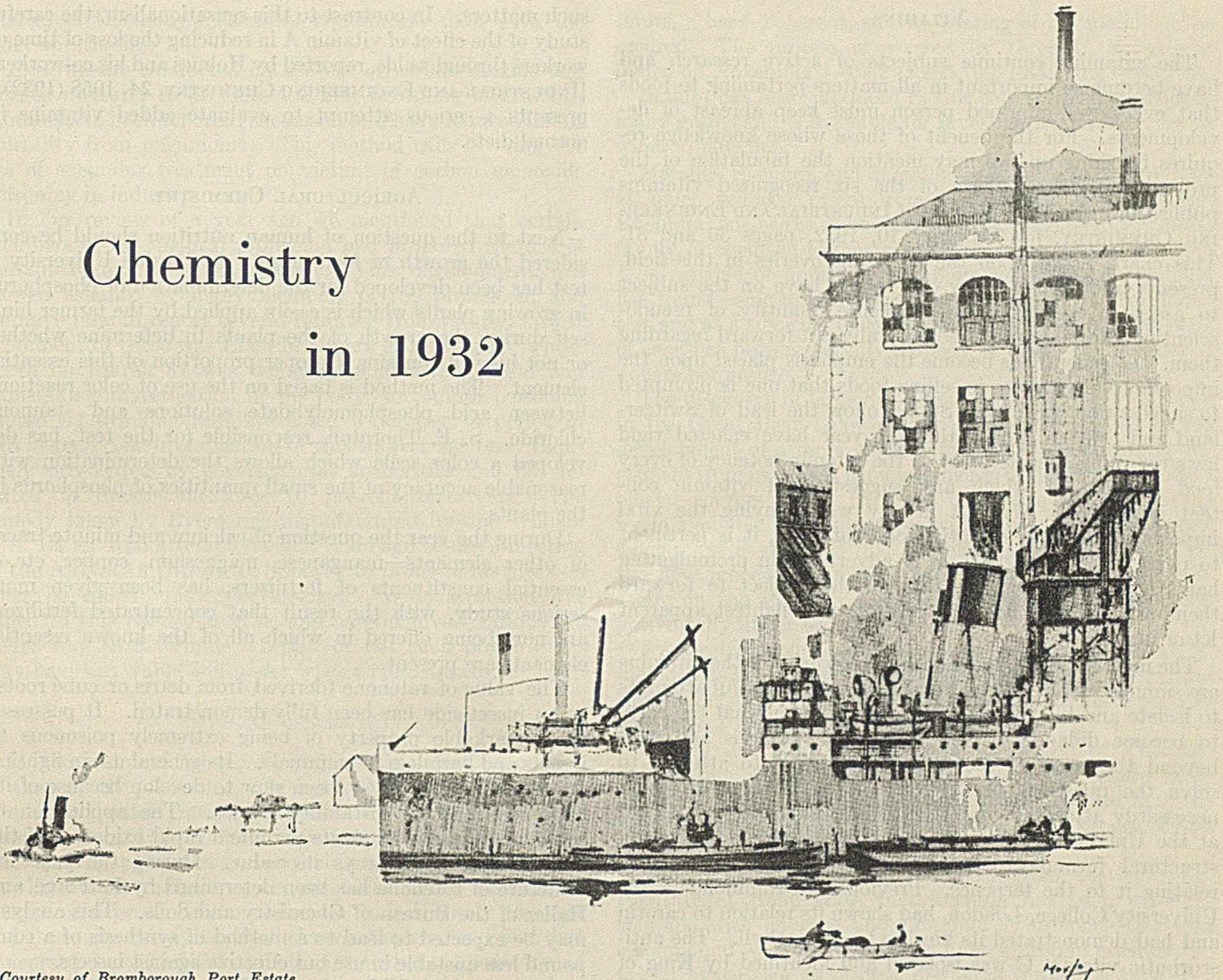
This means that the INDUSTRIAL EDITION, carrying a consecutive number for the editions taken as a whole, will still have its own individual number. Likewise the ANALYTICAL and NEWS EDITIONS, which though they indicate the volume number of INDUSTRIAL AND ENGINEERING CHEMISTRY under the name, will display for their special edition a volume and number consistent with that edition as heretofore known. In this manner we not only comply with the law, but, we believe, avoid confusion in the literature.

∴

OUR ANALYTICAL EDITION. When the ANALYTICAL EDITION was instituted four years ago, we had reason to believe that it would meet a peculiar need which until that time had not been properly served, but its popularity has been greater than we anticipated and the demand for it has grown. Its size has increased as rapidly as funds could be found to support it.

We are happy to announce that the Directors have approved placing the ANALYTICAL EDITION on a bimonthly basis, beginning with January, 1933, and while the volume for the year will be no larger than that which appeared in 1932, we believe those in industrial plants and laboratories generally will welcome this useful tool as it appears in six numbers in place of the customary four. The large amount of material received for consideration is a compliment to the edition, and from it, with the help of reviewers, we shall continue to select that which appears to be of the greatest utility to fill our limited number of pages. With this increased service we believe the edition will go on to even greater usefulness.

Chemistry in 1932



Courtesy of Bromborough Port Estate

• • •

ADVERSE economic forces continued dominant in chemical industry during the past year. The long anticipated recovery of an economic equilibrium has not yet fully materialized, although toward the end of the year many signs were taken to indicate that the slow upswing of business had been started. Fear and uncertainty continued during the year to prevent important industrial developments from taking active shape. In the meantime, progress in research has continued to accumulate the basic ideas and discoveries which will greatly assist in the development of business when courage returns to capital and the wheels of industry are again put into normal motion.

If this were an economic review, it would be necessary to point out that most of the favorable indications now to be seen are somewhat offset by corresponding unfavorable prospects. The overwhelming election of Governor Roosevelt to the presidency accompanied by a general victory for his party in the Congress and a removal of the anomaly of divided responsibility in government is offset by the possibility of derangement of the tariff upon which industry has come to depend. The probable early solution of the prohibition muddle is scarcely likely to overcome fully the dampening effect of the present international debt puzzle. Banks are filled with money anxious for profitable investment but afraid to venture forth into industry. Multitudes of other opposing forces interest the economist in the present situation, and in the meantime he, like the rest of us, must wait with what patience he can until time solves the vexing problem of what is to happen next.

Unemployment among chemically trained workers has shown a small but gratifying decline during the closing months of the year. No large groups, comparable with those of 1931, have been released, and a few bold souls have had the confidence necessary to add to their pay rolls men of special qualifications to assist in developing new processes and new materials to be ready for commercial exploitation when circumstances justify it. The plight of the greater number of the unemployed has not improved with the passage of time. Particularly unfortunate is the situation of the young men released from their formal training during the past two years, who, saddled with debts in securing their educations, have been unable to find employment to help them repay pressing loans. Many of these have found ways to continue their schooling, and the universities find their facilities taxed to meet the demands placed upon them by this situation.

Industries which have been accustomed in normal times to send scouts to the technical schools each spring to gather in the most promising of the youngsters have not only failed to do so but have actually found it necessary to let the scouts go. In general, the openings for men now seem available only for those of special qualifications; others without the required abilities are under an increasingly heavy burden as debts pile upon debts and resources dwindle.

VITAMINS

The vitamins continue subjects of active research and have become so important in all matters pertaining to foods that every well-informed person must keep abreast of developments. For the benefit of those whose knowledge requires brushing up, we may mention the tabulation of the properties and occurrence of the six recognized vitamins published in the News Edition of INDUSTRIAL AND ENGINEERING CHEMISTRY, for February 10, 1932, pages 30 and 31. This chart, based upon the latest discoveries in this field, presents information every one should have on the subject to assist in evaluating the immense quantity of pseudo-scientific information now so generally put forward regarding them. So general has become the emphasis placed upon the importance of vitamins in selling foods that one is prompted to suggest that the United States follow the lead of Switzerland and Sweden, who within the year have enacted rigid laws requiring specific proof of the vitamin potency of every food product for which any suggestion of vitamin content is claimed. Without in any way denying the vital importance of these essential food catalysts, it is pertinent to point out the recklessness of advertisers in promulgating half-truths and misinformation on the subject to forward their own ends, without, at present, the slightest apparent let or hindrance.

The most important advances in knowledge of the vitamins are summarized in several important and successful attempts to isolate and to synthesize them. It is somewhat too early to become didactic on the subject of synthesis and it is beyond the scope of the present discussion to attempt to solve the questions of priority and validity which must necessarily attach to conflicting claims in the field. Karrer at the University of Zurich announced early in the year a structural formula for the growth-producing vitamin A, relating it to the terpenes. Previously, Drummond of the University College, London, had shown its relation to carotin and had demonstrated its kinship to chlorophyll. The anti-scorbutic vitamin C was isolated and identified by King of the University of Pittsburgh and was synthesized by Rygh of Norway, according to announcements made during the year. King isolated the material from lemon juice, long known to be a potent source of it; Rygh produced a material potent in doses of 0.02 milligram to guinea pigs by the acid hydrolysis of narcotine, after showing that narcotine (present in unripe fruit) is replaced by the vitamin as ripening progresses. It is especially interesting to note that both these investigators are young men, Rygh being twenty-eight and King thirty-three at the time of their respective discoveries. Vitamin D, the antirachitic vitamin, has received a great deal of attention during the year from both scientists and advertising men. In Germany Windhaus, in Holland Reerink and Van Wijk, in England Bourdillon, and in the United States Bills and MacDonald—all have announced successful conclusions of their respective researches on the isolation of vitamin D. Zucker of Columbia University reported the discovery of a commercial method of manufacturing a highly concentrated form of this important vitamin.

Numerous commercial preparations containing the various vitamins in more or less concentrated form have been offered in the market, and a great hue and cry has been kept up to make the general public "vitamin conscious." Not the least spectacular of the advertising phases of the matter was the stunt of a publisher especially interested in foods, who paid twenty men and women in two groups to live for thirty days on exclusive rigid diets composed of whole wheat and milled wheat, respectively! Such circus stunts detract materially from the effect of the vast amount of thoughtful, painstaking research that is being directed toward finding the truth in such matters. In contrast to this sensationalism, the careful study of the effect of vitamin A in reducing the loss of time of workers through colds, reported by Holmes and his co-workers [INDUSTRIAL AND ENGINEERING CHEMISTRY, **24**, 1058 (1932)], presents a serious attempt to evaluate added vitamins in normal diets.

AGRICULTURAL CHEMISTRY

Next to the question of human nutrition should be considered the growth of food crops. At Purdue University a test has been developed for the determination of phosphorus in growing plants which is easily applied by the farmer himself during the growth of the plants to determine whether or not his soil contains a proper proportion of this essential element. The method is based on the use of color reactions between acid phosphomolybdate solutions and stannous chloride. S. F. Thornton, responsible for the test, has developed a color scale which allows the determination with reasonable accuracy of the small quantities of phosphorus in the plants.

During the year the question of calcium and minute traces of other elements—manganese, magnesium, copper, etc.—essential constituents of fertilizers, has been given more serious study, with the result that concentrated fertilizers are now being offered in which all of the known essential elements are present.

The value of rotenone (derived from derris or cubé roots) as an insecticide has been fully demonstrated. It possesses the remarkable property of being extremely poisonous to insects and harmless to mammals. Its general use in fighting crop pests has, however, been slow to develop because of its high cost and its instability in use. The application of rotenone solutions to plants permits a rapid oxidation of the material, which destroys its value. During the year the structure of rotenone has been determined by La Forge and Haller of the Bureau of Chemistry and Soils. This analysis may be expected to lead to a method of synthesis of a compound less unstable in use but effective against insects.

Two new insecticides, deguelin and tephrosin, have been developed for use on vegetation in the Department of Agriculture. They cause no injury to the plant and are relatively harmless to human beings.

Results of a long series of researches conducted by the Bureau of Plant Industry have shown that the storage of fruits and vegetables for a short time in an atmosphere relatively high in carbon dioxide checks the growth of rot organisms. This is particularly important in view of the probable early general application of solid carbon dioxide refrigeration to the transportation of fruits and vegetables.

MEDICINAL CHEMISTRY

In the field of medicine two rather important discoveries have been announced during the year. From the University College of Science in Calcutta comes the report of a synthetic quinine which possesses the same antiparasitic value as the natural product but is considerably less bitter. Full information is yet lacking but the synthetic material is reported, on the basis of preliminary experiments, to be probably more useful than naturally occurring quinine.

At the University of California Medical School, experiments in the use of divinyl oxide show it to be a rapid and efficient general anesthetic. The report of this work, confirmed in the University of California Hospital, states that divinyl oxide acts more rapidly than ether or chloroform, and is more rapidly voided from the system than ether, with less excitement and nausea to the patient. Through its use there is less irritation of the lungs, less disturbance of the heart, and less change of the body's chemical equilibrium than with the older anesthetics.

Experiments conducted on the use of carbon dioxide and oxygen mixtures to promote the first breathing of newborn infants have been reported successful and have reduced infant mortality from pneumonia. This method calls to mind the use of a similar treatment on victims of carbon monoxide poisoning in industry.

In our review of a year ago we mentioned that certain members of the medical profession had proposed the use of radium-treated water as a tonic. This development was viewed askance by many members of the profession, and we have now to report several fatalities from its use. Most prominent of these was Eben M. Byers of Pittsburgh, whose death on March 31 was definitely laid, after careful and painstaking investigation of his body, to radium poisoning caused by drinking radium-treated water over a period of two years. The investigation of this subject has been vigorously prosecuted by governmental authorities and has resulted in drastic measures to prevent recurrence. The remedy taken by Byers was manufactured by one William J. A. Bailey who attempted some years ago to use a meeting of the AMERICAN CHEMICAL SOCIETY to promote his ideas on what he called "radiendocrinology." Wide attention was called to this particular case, and careful investigations are under way to determine whether or not such preparations may have any value and under what circumstances.

PHYSICAL CHEMISTRY

In the realm of subatomic physics the latest conception is that of the neutron. The neutron is considered to be a minute particle carrying no free electrical charge. The conception of the neutron was developed to explain extraordinarily penetrating radiation obtained by bombarding beryllium with radiation from polonium. It is assumed to consist of a proton and an electron bound closely together and mutually satisfying their electric charges, and was first conceived by Chadwick in the Cavendish Laboratory of Cambridge University. He found it necessary to postulate such a neutral particle in order to explain some of the phenomena of penetrative radiation which do not fit the accepted views of electrons and protons as charged particles.

Cockroft and Walton, also of Cambridge University, succeeded during the year in disintegrating the lithium atom into two helium nuclei. This result was obtained by bombarding lithium by protons under a pressure of about 125,000 volts. A partial confirmation of this work was made by Lange and Brasch in Berlin, who used voltages up to five million in the laboratory of the German General Electric Company to break up lithium atoms.

From Britain comes the report that the imperial standard yardstick in eighty years has lost 0.0002 inch and that the imperial standard pound has lost one five-millionth of its weight. Slight as these changes seem to be, active investigations are under way in an effort to determine and establish more permanent standards which possibly may be based upon the wave lengths or speed of light.

MISCELLANEOUS

The separation at Columbia University late last year of the isotope of hydrogen from liquid hydrogen by using low temperature methods has been confirmed by workers at the University of Michigan using hydrogen chloride.

Electrodeposition of tungsten, made possible by the processes of Fink, adds this metal to the ever increasing number of corrosion resistants. By using a solution containing alkali tungstates having a pH of about 12, and carefully controlling temperature and current density within narrow limits, a hard, coherent, smooth coating of the metal can be secured. The process is covered by three U. S. patents issued on November 1, 1932 (1,885,700, 1,885,701, 1,885,702).

Indium has been produced in this country in quantities of many grams and is available for investigation with a view to wider application.

Metallic rhenium and metallic gallium are offered here at much reduced prices from the German manufacturer. Rhenium, one of the most recently discovered members of the family of chemical elements, possesses great hardness which it is capable of imparting to alloys containing it; gallium has found some application in high-temperature thermometers and as a silvering metal for mirrors. Although the price of each has been materially reduced, it is still of the order of dollars per gram.

The discovery of large deposits of radium-bearing minerals in the Great Bear Lake district of Canada has led to the development of a more efficient method of extraction of the element from its ores. Announcements of this from Canadian official sources imply that the quantities of radium thus made available are comparable with those from the Belgian Congo. It is expected that the efficiency of production by the new process will make Canadian radium an important factor in the market. Commercial operation has not yet gotten fully under way.

By spectroscopic observations and measurements, carbon dioxide has been discovered in the atmosphere of Venus, and astronomers are led to believe that this may indicate possible evidence of life there.

Helium has been discovered in the island of Trinidad. Information is still scanty on this discovery (made while drilling for oil), but reports indicate that Trinidad may become a substantial contributor to the world's supply of this rare gas.

Reports received late in the year from the Chemical Institute at Bonn state that krypton has been made to combine with chlorine and bromine. The conclusion that a compound was formed is based upon a drop of pressure obtained by passing an electric discharge through a tube containing chlorine and krypton, at low temperature and pressure. The observers obtained a dark red compound which they believed to be krypton chloride.

From the Pasteur Institute in Paris comes the announcement of a new type of filter possessing extraordinary power of destroying common bacteria. It utilizes the oligodynamic effect of silver and is constructed by introducing silver chloride into clay before firing. The resulting filter has metallic silver distributed through its interstices in finely divided form. Water filtered through the device has no detectable amount of silver in it, yet it retains its germicidal value for several days afterward, according to Georges Lakhovsky, its inventor.

A new corrosion-resistant coating material formed by the polymerization of divinyl acetylene has proved to be remarkably resistant to chemical action and efficient as a protective coating. Unlike natural drying oils this material hardens by polymerization rather than oxidation. The process and application are covered by U. S. patents 1,812,544 and 1,812,849 of June 30, 1931.

INDUSTRIAL DEVELOPMENTS

The low prices reached by silver and platinum during the year place them more easily within the reach of chemical industry for the construction of equipment utilizing their valuable properties. With silver as low as 24$^7/_8$ cents an ounce (\$2.98$^1/_2$ per troy pound), it can be used for equipment for processing food products and for heat transfer more generally than ever before. This price is noted as the lowest ever reached by silver, and the manufacturer who invests in equipment built of it can be reasonably sure that its value will increase rather than diminish in service. Similarly, the price of platinum has dropped to startlingly low levels and is now quoted at $32 per ounce from an accustomed level of over $100.

During the year a licensing arrangement has been made with fifteen of the more important petroleum refiners to use the hydrogenation patents owned by the Hydro Patents Company, formed for the purpose. These patents cover the hydrogenation of petroleum and are based on the original coal-hydrogenation patents of Bergius. This makes available to the American petroleum industry generally this latest development in petroleum refining.

A new machine for making gas from anthracite coal has been developed by the Anthracite Institute. Preliminary estimates put forth by the Institute state that the probable cost of gas of the proper quality for domestic use for fuel will be about 20 cents per 1000 cubic feet, including all charges except distribution. This development is the result of research undertaken by the anthracite coal industry to regain its lost markets.

White paper from southern yellow-pine forests has become an actuality as a result of successful experiments conducted by Herty on this subject. The method of treatment developed for this purpose makes available huge pine forests in the South which previously could not be used for making paper. Numerous samples of various grades of white paper have been prepared and have clearly demonstrated the possibilities of paper making from this raw material. Commercial operation has not yet been started.

A new method and machine for pretreating potters' clay have been developed and put into operation during the year. The process removes air or other gases from the clay body by alternate applications of vacuum and pressure, and yields an extremely dense and uniform product. The value of this treatment has been demonstrated by the increased tensile and compressive strengths of the ware both before and after burning, and by the uniformity of the body of the finished product from the kiln. It avoids blisters and cracks which cause the rejection of a considerable proportion of articles fired from clay prepared by the ordinary method. Extensive researches carried on by the Ohio State University Engineering Experiment Station have fully upheld manufacturers' claims.

The prospective repeal or modification of the Volstead Act to permit the manufacture of beer has already led to the revivification of several of the old brewers' academies and to the formation of new ones. The probability of larger requirements of plant equipment to rehabilitate the brewing industry has caused many manufacturers to initiate new lines to meet the demand.

Several important developments which have proved their value abroad have been brought into this country and are being put into operation here. A synthetic plastic capable of being formed into useful shapes without the extraordinary cost of huge molds has been imported from Germany. We are told that pieces of equipment as large as 10 feet in any dimension can be successfully molded from this material at a cost comparable with that of some of the stainless alloys. The finished equipment is highly resistant to all nonoxidizing acids.

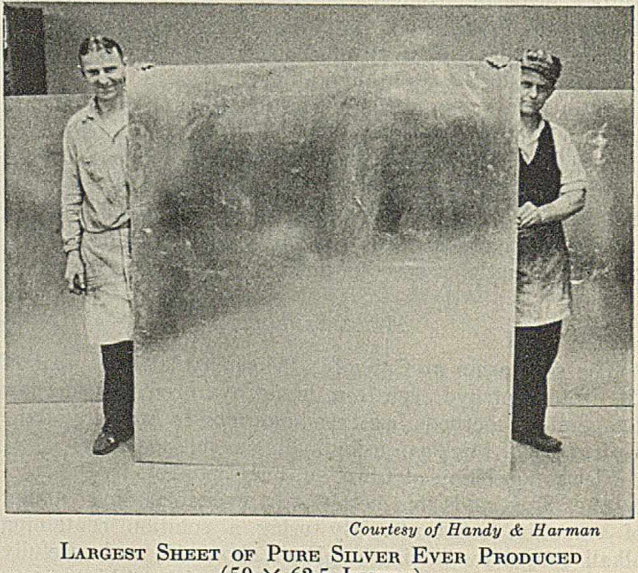
Arrangements have been completed for the manufacture in this country on a large scale of the alcohols corresponding to the common fatty acids and their sulfuric acid derivatives. These materials have been found to possess unusual efficiency as cleansing agents to replace soap, and to possess none of soap's drawbacks. The process consists of the direct hydrogenation of fatty acids to the alcohols and the sulfonation of these to easily soluble compounds.

Soviet Chemical Industry

Chemical aspects of the Soviet plan of development of Russia's natural resources continue interesting despite the lack of complete and reliable information about them. Early in the year a change of policy caused by the reduced foreign credit of the Soviet Government resulted in the loss of a number of American engineers to developments there. The original plan upon which foreign brains and ingenuity were put to work in Russia involved the payment to selected persons of a substantial part of their salaries in gold to be placed to their credit in the United States or elsewhere as designated in contracts made. The remainder of the salary, presumed to be ample to permit comfortable living in Russia, was to be paid in rubles which are practically worthless outside the Soviet. The rising cost of foreign money, particularly dollars, led to a change in this respect and the repatriation of a considerable number of foreign experts.

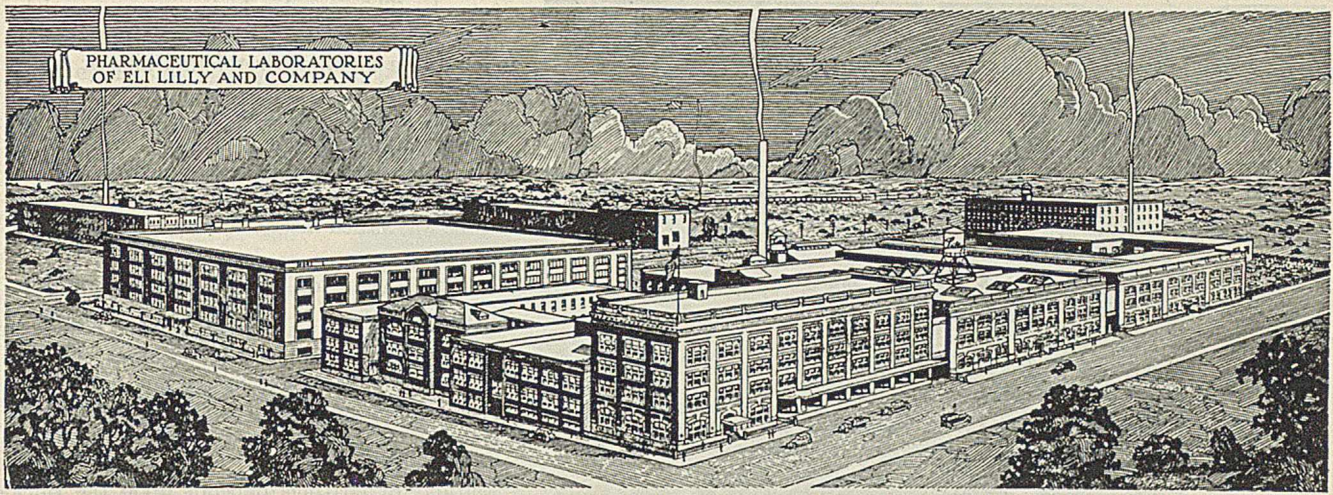
In the meantime, developments have proceeded as rapidly as the situation allowed, and according to some reports a substantial chemical industry is being built up. Large natural deposits of carnallite are being worked for compounds of potassium and magnesium as well as metallic magnesium. Coal distillation and the elaboration of coal tar are in production. The fundamental requirements of the chemical industry for acids and alkalies are being met. Synthetic rubber is reported to be in prospect within the near future as plants for its production approach completion. Fertilizers and electrochemical products (chlorine, bromine, and caustic soda) have already been provided to meet the demands of the country. These developments have been watched with special interest from this side of the Atlantic because of the potential threat to our world trade involved in the creation of another large national chemical industry.

Critics of the whole scheme suggest failure at every turn and doubt the soundness of progress reported. They point out the enormous natural difficulties of climate and distances, of general ignorance and scanty resources, which must doom the development and which cannot be overcome by fiat. On the other hand, a fair-minded view of the situation as the original five-year period nears its end must recognize remarkable accomplishment in the creation of any industry under such severe handicaps, entirely aside from the political aspects of sovietism and communism.



Courtesy of Handy & Harman

Largest Sheet of Pure Silver Ever Produced
(59 × 62.5 Inches)



Indianapolis Laboratories of Eli Lilly & Company Where Twelve Distinct Air-Conditioning Plants Are in Operation

Air-Conditioning in the Drug-Manufacturing Industry

William A. Hanley, Eli Lilly and Company, Indianapolis, Ind.

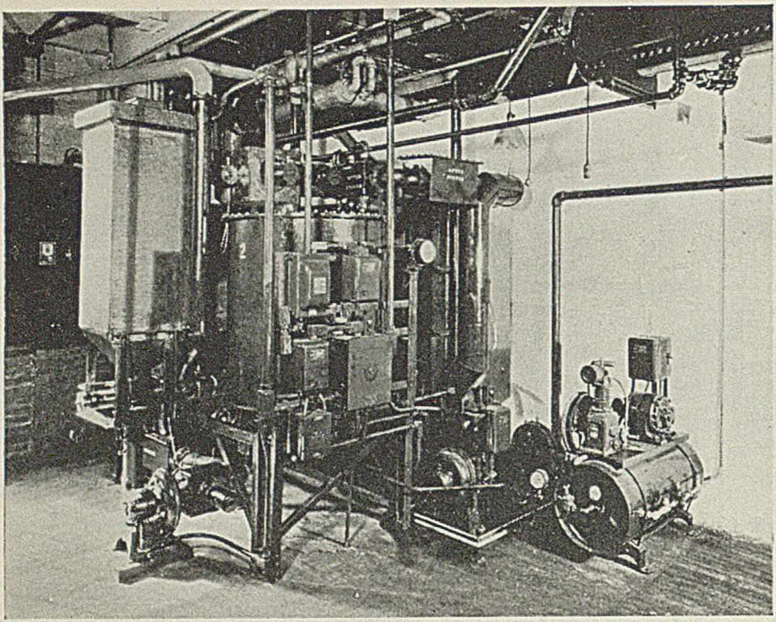
When we speak of air-conditioning in the manufacturing industries, we mean the treatment of air so that the temperature, the humidity, the volume, and the velocity are controlled. Heated air, in unknown volumes with little regard to temperature and no regard to humidity, has been used in the drug-manufacturing industry for centuries. It would be hard to trace the origin of the ordinary drying closet or hot air chamber. Heat and circulation of air seemed to be the only requirements. Shortly after the close of the nineteenth century, air-conditioning came into the drug-manufacturing field. Its importance and application have increased not progressively, but about as the square of the years since 1900.

It is related, and on good authority, that a certain large pharmaceutical manufacturer, struggling to make gelatin capsules (a process always fraught with many difficulties), sent for the engineer of a fan manufacturer and asked him to assist in working out the process of drying. The young engineer, after some study, realized that only an apparatus which could turn out air with a fixed temperature and humidity would satisfy the job. Being a genius, he conceived that humidity could be controlled by passing the air through sprays of water; by thus cooling, he could reduce the moisture content to the desired point. Accordingly, the young engineer designed an air washer and convinced his customer that it would do the work. The customer asked for the usual guarantees of performance, but the president of the fan company was reluctant so to bind his corporation. The result was that the drug manufacturer took the plans and built the air-conditioning unit, which did all that the engineer claimed it would do. The engineer left his job with the fan company, organized a corporation to make air-conditioning equipment, and has ever since been one of the largest factors in the development of the industry.

Manufacture of Capsules

Of all jobs of conditioning air in the drug business, the matter of capsules undoubtedly presented the greatest difficulties. The wall of a capsule varies in thickness from 0.003 to 0.006 inch, depending upon the size of the capsule. The smaller capsules must not have a wall thickness over 0.0035 or under 0.0025 inch. If the wall is thinner, the capsule is too fragile; if thicker, the caps will fit too tightly on the bodies of the capsules. To work within these close limits in addition to controlling the viscosity and temperature of the gelatin to be molded, the temperature of the pin on which the capsule is to be molded must also be controlled. This is part of the role of the air-conditioning plant. Another job of the same plant with the same air at the same time is to set the gelatin on the capsule pins immediately after the pins have been dipped into the molten gelatin. Again, the same air must dry these capsules in forty-five or fifty minutes so that they can be stripped off the pins on which they have been molded. For different sizes of capsules, different temperatures of air are required; but the moisture content, measured in grains per cubic foot of air, can be constant for the same gelatin. Close regulation of the air-conditioning plant is necessary, as the moisture content of the air should not vary over 0.25 grain per cubic foot, and the temperature not over 0.5° F. This is not easily accomplished when 30,000 to 60,000 cubic feet of air per minute are conditioned. In case of both humidity and temperature, a departure above or below the fixed limits causes trouble. In many processes an upper or a lower limit alone is set, but with capsules both an upper and a lower limit are fixed for humidity and for temperature. The process is a closed circuit wherein the conditioned air is fed to the capsule machines, is then dissipated in the insulated capsule-manufacturing room, and is then returned to be reconditioned. A washer, using water, cooled by refrigerating machines, and controlled automatically to meet all weather conditions, has made capsule manufacturing continuous and satisfactory.

Although the conditioning of air for capsule manufacture was one of the most difficult of application, it has brought large returns both to drug manufacturers and the air-conditioning industry. Before the use of conditioned air capsules



Plant for Supplying Especially Dry Conditioned Air in Lilly Laboratories

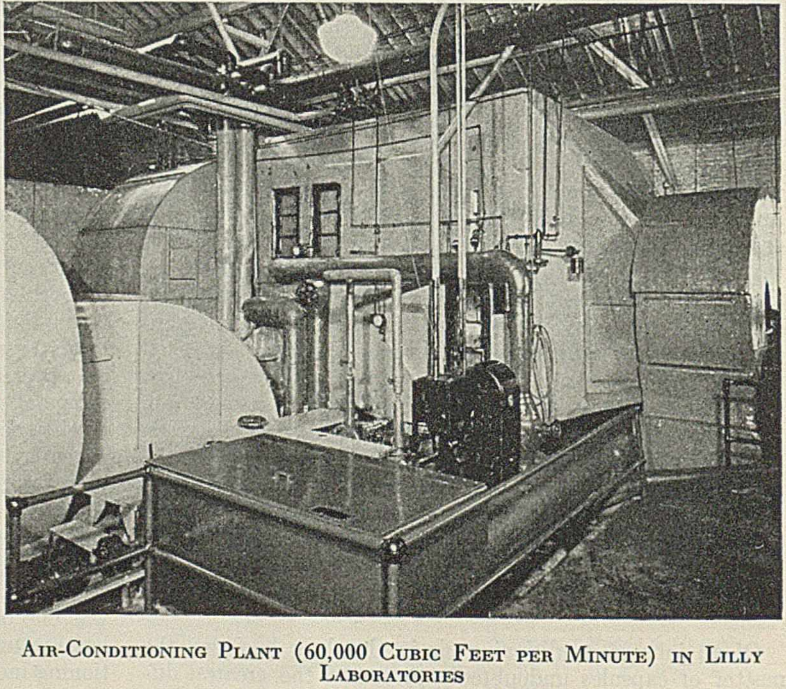
could not be made during the summer, so that the drug manufacturers were obliged to suspend operations sometimes for two or three months a year. Capsule-manufacturing equipment stood idle, and employees had to be assigned to other work or be temporarily suspended. Equipment had to be installed to take care of twelve months' demand in nine months' operation. This, however, was not the whole story. There are always days from April until November when the weather is warm and humid. Such days coming once or twice a month meant trouble in manufacturing capsules and very often the spoiling of a batch of gelatin. Since gelatin costs from 40 cents to $1.25 per pound, losses amounting to several thousand dollars were often encountered because of suspended operations and spoilage of gelatin. Proper air-conditioning has made possible the continuous manufacture of capsules every working day of the year. Owing to this continuity and to the standardization of drying and conditioning, the annual output of the same capsule machines is two and one-half times what it was before the advent of air-conditioning. The conditioning of air for manufacturing photographic film was receiving much study about this same period, and the findings in the researches on one were quite useful in the researches on the other.

Although the conditioning of air for capsule manufacturing was expensive and difficult, and represented a large investment for the drug manufacturer, much research for the engineer, and the development of some fine control apparatus, it had its reward, for it opened a field for air-conditioning which has proved profitable to the drug manufacturer and to the builders of air-conditioning apparatus. The drug manufacturer, who had experienced trouble with pills and tablets which were improperly dried or stored, immediately began to study the factors which seemed to bring about such troubles. It was thus that case-hardening, or the drying of the outside skin of a pill or tablet, was soon understood. This case-hardening was caused by drying in air of too low moisture content. Thus the manufacturer found pills or tablets which had been bottled 6 months giving off moisture and becoming a sticky mass. With air-conditioning and properly controlled apparatus the drying was retarded until the core or center was dried first, so that no moisture was sealed inside.

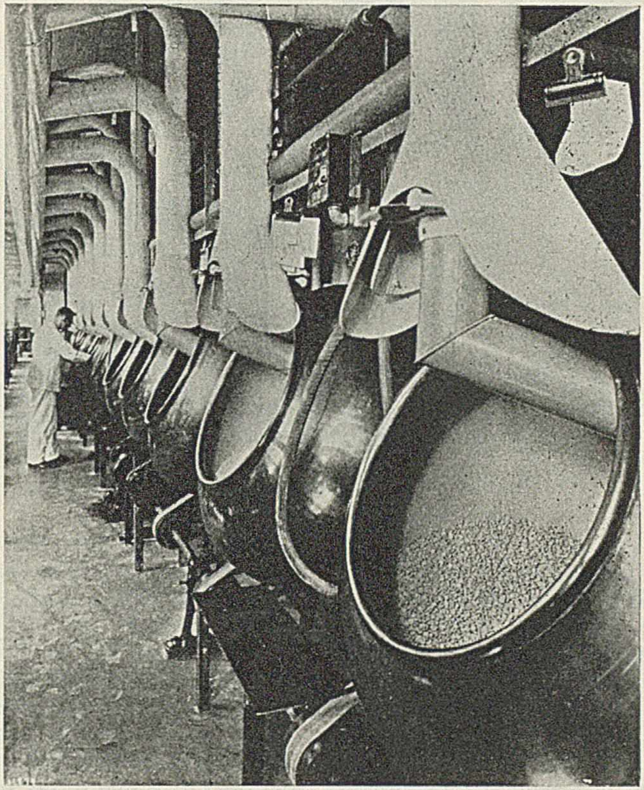
Coating of Pills and Tablets

Air-conditioning also contributed largely in the solution of coating of mass pills and tablets. In such coating the liquid is applied to a tumbling mass of molded centers, chocolate, or other coatings in liquid solution at definite temperatures. The number of applications or coatings depends upon the thickness of built-up coating desired. In this continuous process the absorption of moisture should be uniform. The dry-bulb temperature should be held quite constant; of even greater importance is the wet-bulb temperature, since the mass will vary in volume with the wet-bulb temperature in the same manner that a wet-bulb thermometer expands or contracts.

The air-conditioning of pills and tablets brought with it not only the standardization of temperatures, humidities, and velocities, but also the uniform distribution of the air and the uniform drying of all the tablets or pills in the same lot. To assist in this uniformity, it has been found advantageous to move the racks containing the trays of pills and tablets slowly through the dry houses so that each tray or rack meets the same conditions in the drying cycle. Air-conditioning and its controls can also take credit for doing away with scorching or burning of pills and tablets, because controls for air temperature were not made satisfactorily until the air-conditioning industry brought out such instruments. The drying of pills and tablets under standardized conditions has permitted accurate scheduling of operations which hereto-



Air-Conditioning Plant (60,000 Cubic Feet per Minute) in Lilly Laboratories fore were uncertain. It has done away with guessing and rule-of-thumb standards, and has substituted methods based on scientific investigation. The manufacture of one particular line of tablets was revolutionized by air-conditioning. Effervescing tablets, or those tablets which give off large quantities of carbon dioxide when submerged in water, were formerly made in only three months of the year—December, January, and February. Even in these months the tablets often contained enough moisture to be useless when the bottle was opened. This manufacturing and bottling is now done in air-conditioned rooms; where proper conditions can be maintained, the manufacturing can be carried on any day of the year. For effervescing tablets the moisture content of the air should not exceed 15 per cent relative humidity at 90° F. This is a moisture content found only on dry cold winter days. For this reason the work required of the washer and refrigerating machines justifies tightly sealed and carefully insulated conditions.



Conditioned Air Being Supplied to Coating Pans in Lilly Laboratories

Manufacture of Gland Products

In the manufacture and processing of gland products, air-conditioning has played an important part. Gland products are expensive, are subject to contamination, and spoil if not given the best of treatment. The therapeutic value of many glands and other animal products is totally destroyed by processing at a temperature above 25° or 30° C. (77° or 86° F.). Air-conditioning, particularly during the summer months, has greatly reduced this hazard and stopped many of the losses.

Conditioning of Animal Quarters

Another application which the drug manufacturer has found to be profitable is the conditioning of animal quarters. Large numbers of animals, such as guinea pigs, white mice, rabbits, chickens, cats, and dogs must be used in pharmacological testing and in the research work so necessary to advance the art of medicine. Some animals are susceptible to certain diseases, especially pneumonia, and all animals have lessened resistance under certain circumstances. It takes no stretch of the imagination to estimate the consternation wrought in a research laboratory, when a group of animals under careful observation are found dead. The work of several scientists for six or eight months may be entirely wasted. The development of some new product may be delayed for a year. All animal quarters do not need air-conditioning, but where the animals are debilitated or weak, or where slight changes in temperature or humidity introduce variables in research, the conditioning of animal quarters has been found profitable.

Drying of Bottles

Years ago bottles were washed either by hand or on rinsing machines, and were then stacked in trays and put in ordinary drying closets, where air circulation and heat made them bone-dry in a period between three hours and three days. The air-conditioning industry, with the conveyor manufacturer, reduced this drying time to thirty minutes and consequently saved many dollars in floor space and in investment. The bone-dry bottle is just as dry today in thirty minutes as it was after the three-day period in use twenty-five years ago. In the industry it is almost universal practice for the manufacturer to wrap bottles in parchment paper to protect the label and to keep the bottle clean. In a dry cold atmosphere the parchment paper shrinks and cracks and fails to give the anticipated protection to the label. With simple apparatus and small cost the air can be so conditioned where the wrapped bottles are stored that the package can leave the plant of the manufacturer entirely unimpaired.

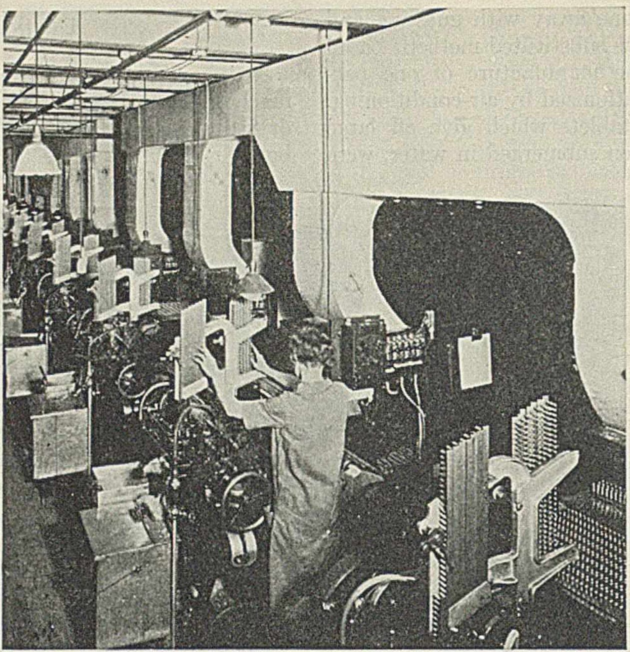
Use of Air of Low Humidity

In all large pharmaceutical plants there are processes, some public and some private, where air of extremely low moisture content is required. Some of these processes use air of as low as 5 per cent relative humidity at normal temperatures. No such conditions were obtained except in a small and limited way before the advent of modern air-conditioning. Although costly to attain, air can be had and is being used with this low moisture content. There seems to be a definite point (around 12 or 15 per cent relative humidity) below which it is cheaper to take out the moisture by absorption with materials such as silica gel than by the process of reducing the temperature of the air in a washer. It would seem that the field, although limited in application, is open to further development.

Equipment for Air-Conditioning

In air-conditioning in the drug-manufacturing industry, the type of equipment does not differ greatly from that used in cooling theaters and office buildings. Usually a washer of the horizontal pass type is installed, where the air quantity is large, with the usual standards of air velocity and with nozzles, eliminators, and circulating pumps. Whether or not the washer will be insulated, and to what extent, depends entirely on the temperatures of the water or brine used in the washer. Where the air is heated after being washed, considerable refrigeration can be saved (if the heating is an appreciable amount) by the installation of an interchanger which warms the air after leaving the washer, by means of taking heat from the air about to enter the washer. Simplicity of parts and accessibility for cleaning and adjustment are quite necessary in air-conditioning equipment. A washer is fundamentally a collector of dirt and dust, and should be so designed as to get rid of all mud and be easily cleaned, preferably without interrupting its operation. The early type of small washer nozzles was a trial to the operator, but these have all been largely replaced by nozzles of larger bore.

Although it is true that there are some large central air-conditioning units installed in drug-manufacturing plants, as a rule the smaller unit especially designed for one application or process is most satisfactory. Large duct work is expensive to build and insulate and often takes space to the detriment of manufacturing operations. A small compact plant, immediately alongside and above or below the room to be conditioned, seems to be most satisfactory. Temperatures and humidity are then controlled for one purpose or process only, and the conditioning plant can usually be operated by the person responsible for the manufacturing operation. Divided responsibility is thus avoided, and usually under such circumstances the conditioning equipment receives better maintenance because the manufacturing process is dependent upon good operation of the conditioning unit. In many manufacturing operations an interruption of service is costly, and for that reason the best of maintenance is justified. Washer screens should be changed daily, or oftener when conditions indicate. Nozzle pressures should be checked daily, or hourly if the process involves expensive materials. The washer should be thoroughly flushed out at least once a week and should be filled with clean water every two or three days. Annually the entire plant should be examined, cleaned, and painted. If such precautions are taken, the washer casing, eliminators, fan runner, and pumps will last under ordinary conditions for fifteen to twenty years.



Capsule-Manufacturing Machines in Lilly Laboratories

Conditioned air is supplied from overhead ducts.

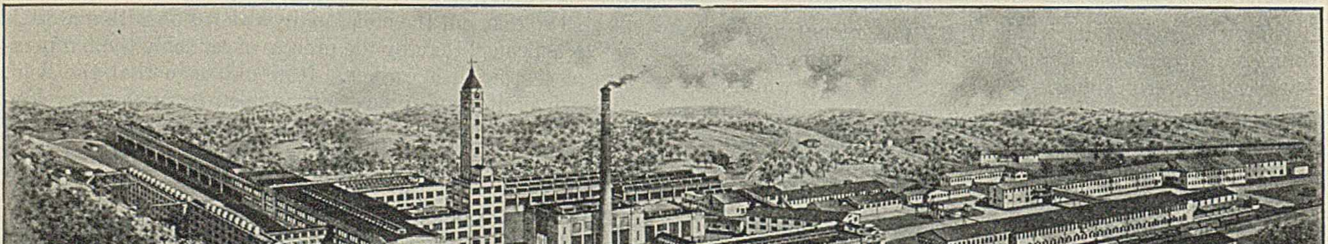
In most instances washers can be made of galvanized or black iron, fans of steel plate, and pumps of cast iron. Copper, monel metal, stainless steel, and bronze pumps can be used when necessity demands, but this is seldom the case in the drug-manufacturing business.

Any process which justifies conditioned air also justifies recording instruments, so that there can be established an unquestioned record of performance of the conditioning plant. These recorders should be checked monthly for accuracy.

Conclusion

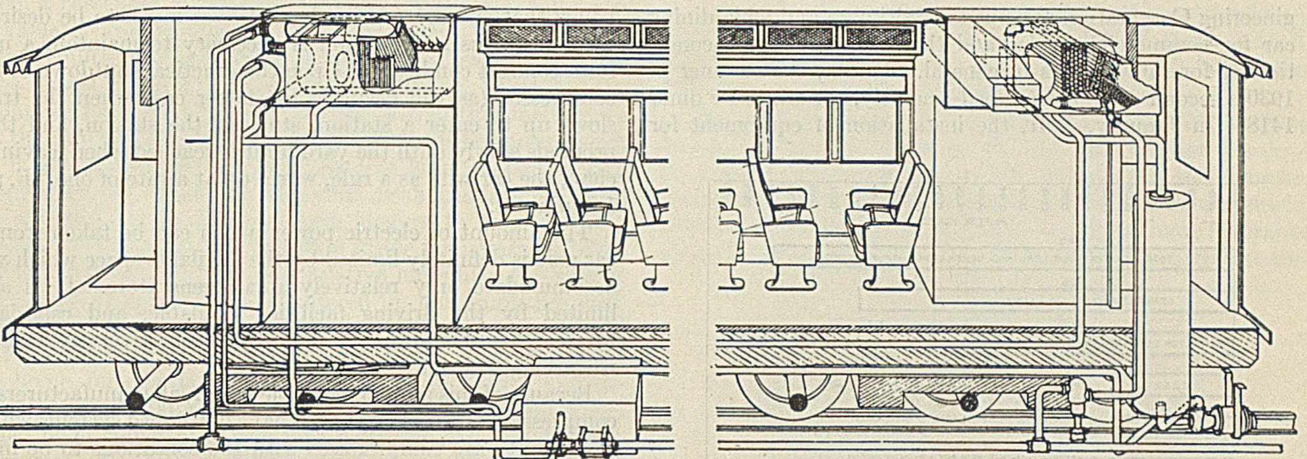
Many important drug-manufacturing processes are not affected by atmospheric conditions, particularly those carried on with liquids, and in such work as milling, distilling, and concentrating. However, where conditioned air is needed and used, it simply takes several variables which may play an important part in any process, and reduces them to constants. Accordingly, results which have been variable become constant, and constant unfailing results are the final aim of those responsible for manufacturing. The use of conditioned air is playing an important part in the drug-manufacturing industry, and, as time goes on, its importance will undoubtedly increase.

Received October 20, 1932. Presented before the New York Section of the American Chemical Society, New York, N. Y., October 14, 1932.



Present Home of the Peters Cartridge Company, Kings Mills, Ohio

For forty-five years this company was housed in one small building.



Installation of Steam Ejector System

Air-Conditioning for Railway Passenger Cars

H. K. Williams, The Safety Car Heating and Lighting Company, New York, N. Y.

THE development of air-conditioning for railway passenger cars has not been predicated upon humanistic or altruistic grounds, for if it had been, what is an actuality today would still be a dream of the future. Railroads are keen to adopt anything which promises to increase revenue, and increased comfort will without doubt attract more revenue-producing passengers. Air-conditioning does make for comfort in a railway journey, not only in the hot sultry midsummer season but on the coldest day of winter. Until now, every one has dreaded a railway journey in summer. The discomfort incident to heat and humidity is intensified by the dirt and noise which make their entrance to the coach in direct proportion as the crew exerts itself to provide adequate cooling by increasing deck sash and window ventilation. Only those who have ridden on air-conditioned trains can appreciate the effects produced on the average passenger. The delightful coolness, the dryness, cleanliness, and absence of noise in an adequately cooled car are so invigorating and refreshing that the passenger actually dreads to leave the train whereas formerly he dreaded to enter it.

Economic Factors in Air-Conditioning

What are the economic factors which have caused railroad managements throughout the land to seek ways and means of adopting the benefits of air-conditioning? Between 1920 and 1929 (two years of relative prosperity) the net passenger earnings of the class 1 railroads of this country declined by $415,000,000. For two years of relative depression, ten years apart (1921 and 1931), the decrease was $603,000,000, equivalent to 52 per cent. A more illuminating picture of the magnitude of this sum may be conveyed from the fact that $603,000,000 per annum is sufficient to pay 2.5 per cent net return on the entire investment in railway property in the whole country. This enormous shrinkage in the passenger earnings of our railroads makes it impossible for them to earn a reasonable return in ordinary years, or come anywhere near meeting their fixed charges in lean years. The greatest of all problems confronting the railroads today is to get the traffic back on the rails, and every nerve is being strained to that end. One of the most promising means now seems to be the adoption of air-conditioning.

Railroads need recover but a small part of what has been lost to make the adoption of air-conditioning worth while. There are only some 35,000 passenger cars in regular service on steam railroads in the country. With any sort of volume production, $7500 would be an outside price of the system (plus application); thus to equip all the cars in the country would not cost more than $263,000,000, which is less than half of the annually lost passenger earnings. Earnings, not passenger revenue. If but one-fifth of the earnings could be recovered, the equipment would pay for itself in a little over two years.

Men who have made intensive studies of the subject hold the opinion that much of the lost earnings can be easily made up. Opinions, however, are of doubtful value if not supported by concrete evidence. A guest speaker is reported to have stated before a meeting of the South and Southwestern Railway Club[1] that the Baltimore and Ohio Railroad, operating a completely air-conditioned train between New York and Washington, D. C., was able during the past summer to increase the daily average number of passengers between the two points from one hundred to five hundred. A study of the remarks made indicates that the four hundred fares gained daily came from two sources. Approximately two hundred were taken from a competing railroad and two hundred came from people who had not been using railroad service before. The price of a ticket between the two points is roughly $10.00; thus the Baltimore and Ohio Railroad increased its daily revenue by approximately $4000. The competing railroad lost $2000 daily, but the railway industry as a whole gained $2000 per day in revenue. The point of vital interest is that this particular application did increase the passenger travel between the two points by approximately 50 per cent. The figures given are probably accurate, for they were reported by an authority in a position to know the facts.

Commercial use of air-conditioning for railway passenger cars is only two years old. During the summer of 1929 the Carrier Engineering Corporation equipped a Baltimore and Ohio day coach for experimental purposes. The results were encouraging. In the early spring of 1930 the Carrier En-

---

[1] Beach, R. L., *Proc. South & Southwestern Railway Club*, 21, No. 18 (1932).

gineering Corporation equipped a Baltimore and Ohio dining car for commercial service and thus inaugurated air-conditioning for railway cars in general. During the summer of 1930 a second car was equipped—namely, the Sante Fe diner 1418. In January, 1931, the installation of equipment for three Missouri-Kansas-Texas diners was begun. These examples pointed to the feasibility of air-conditioning applied to passenger cars.

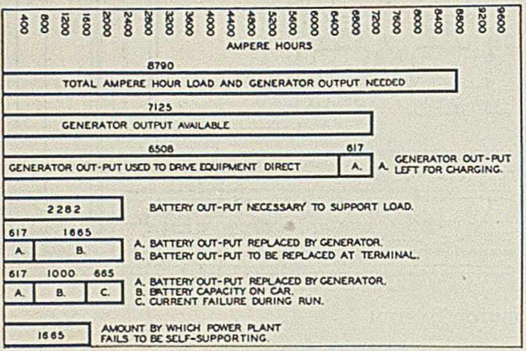


Figure 1. Power-Plant Load Balance for Compressor System Utilizing Freon

Since that time, development of apparatus to accomplish the purpose has received much attention, and considerable study has been made of the type of refrigerant. Almost every fluid known has been investigated. At first ammonia was used exclusively, chiefly because equipment was already available for its use, and because it had desirable qualities from the power standpoint. It did, however, lack the safety attribute. Today no manufacturer advocating compression systems uses anything but dichlorodifluoromethane, commonly known as F-12 or Freon. Despite the disadvantages in practical use of this refrigerant from the power standpoint, it does have the desirable safety characteristics so essential on a moving vehicle where human life is in the balance. For the same safety reason, internal combustion engines for producing the required power are out of the question, although for the entire season of 1931 one railroad did operate thirty-nine cars equipped with gasoline engine drives. At the end of the year, however, they were removed because of the hazard pertaining to their use and because of their high maintenance cost.

At the present time, there are 357 air-conditioned cars of various classes which utilize three types of equipment—namely, mechanical compressors, steam ejectors, and ice melting systems.

Compression Systems

Of the manufacturers now offering electrically driven compression systems to the steam railroads, only two have provided any means of securing the necessary driving power which, upon a moving train up to the present time, can be obtained from but one source. This power source is the one most generally advocated and utilizes a direct-current generator driven from the car axle in conjunction with a stand-by storage battery. Another method of obtaining power for a compression system is offered by a certain manufacturer in conjunction with his system of air-conditioning. This method is a means for driving the compressor directly from the car axle through a magnetic coupling which slips above a certain car speed, thus allowing the equipment to run at a constant rate after this car speed is reached. Such a system operates only while the train is moving above the predetermined train speed, and results in no real useful refrigeration below that speed. Obviously, it leaves much to be desired, for continuous refrigeration is necessary to maintain a uniform comfort condition. Upon the practical shutdown of the compressor (as will occur in the latter case when the train slows up to enter a station, stops at the station, and then proceeds slowly until the yard limit is reached when leaving a city), the car will, as a rule, warm up at a rate of one ° F. per 1.5 minutes.

The amount of electric power which can be taken from a car axle is definitely limited by the available space which will accommodate only relatively small generators. It is also limited by the driving facilities available, and especially by the added load imposed upon the locomotive, particularly when long trains are considered.

Because of this limited available power, all manufacturers of compression types (except one) have developed systems which in actuality are compromises with the conditions to be met. We find advocates of relatively high temperatures with relatively high air velocities; the theory is that high velocities will produce the necessary comfort effect because of rapid evaporation from the skin. High air velocities are not feasible, even with the higher air temperatures considered, because of draughts. Some manufacturers provide facilities for the intake of the 500 odd cubic feet per minute of outside air necessary for a loaded passenger car, but the train crew must cut down the intake close to nothing, because that is the only way the inside temperatures can be maintained adequately. Manufacturers advocate a fairly well-fixed differential between the outside temperature and the temperature to be carried inside the car, and attempt to fix it at 15° F.; thus with outside temperatures at 100° the inside temperature would be 85° F. It is argued that 85° inside temperature with 50 to 55 per cent relative humidity is comfortable, and any greater differential between inside and outside temperatures causes shocks to the passenger which should be avoided. The unfortunate part of this theory is that you cannot convince the passenger that he is comfortable when the temperature is above 80° F. The experience of this company is that the traveler is not happy if the thermometer rises above 75°. The queer part of this theory is that the same people who argue the effectiveness of temperatures higher than 80° F. advocate the use of the equipment to bring the inside temperature down to 72° when the outdoor temperature is 80° with a relative humidity as low as 55 per cent. If 80° +, with 55 per cent relative humidity, is quite all right and actually comfortable during some periods, why use the equipment at all when those conditions can be obtained by merely bringing in untreated outside air?

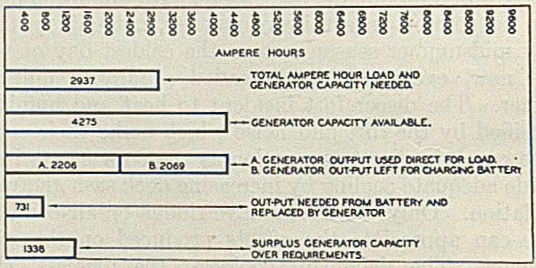


Figure 2. Power-Plant Load Balance for Steam Ejector System

The facts are that no manufacturer of air-conditioning apparatus yet knows how to produce adequately and economically the power needed, and all systems using compressors (except one) are compromises with the conditions met in practice.

Under normal outdoor conditions the heat to be extracted from a passenger car carrying forty or fifty people, will reach a value of around 60,000 B. t. u. per hour. To remove this heat requires refrigeration at the rate of at least 5 tons, but this leaves nothing for abnormal conditions. Test results, using ice for the cooling effect, have proved that melting ice at the rate of 7 tons in 24 hours will at times be encountered. It is not advocated that an equipment large enough to give perfect results under the abnormal peak conditions should be adopted, but it does not seem illogical to believe that a system to be adequate to maintain inside temperatures below 75° F. with 50 to 55 per cent relative humidity, throughout the range of conditions encountered on our trunk line railways, must have available a minimum of 6 tons. The largest field for these equipments is Pullman cars. These cars have no home, for one day a Pullman may be in Florida and the next week in Maine, and equipment suitable for such cars must be of sufficient capacity to meet the normal maximum requirements. Compressor equipment of 4 to 4.25 tons capacity is hardly large enough for universal application, and to develop power for anything larger would be an extremely difficult if not altogether impossible task.

There is but one compressor system now produced which can be considered to have adequate capacity for universal application to meet the imposed requirements. That is a 6-ton system and with it is offered a 15-kilowatt, 38-volt direct current generator to be driven from the car axle by means of gears. This generator, in conjunction with a 1000-ampere-hour battery is expected to carry the refrigeration load of 11.25 kilowatts plus the lamp load which is now ordinarily carried by a 4-kilowatt generator. The normal continuous lamp load is about 30 amperes.

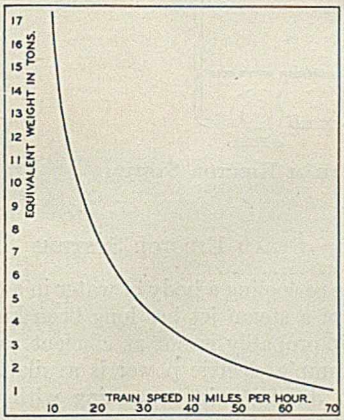


Figure 3. Equivalent Weight per Car Which Could Be Moved at Given Speed by Drawbar Pull Necessary to Generate 1 kw. in Power at Axle

Sample Calculation: Drawbar h. p. necessary to keep 1 ton of car weight moving at constant speed varies with rate of speed. At 40 m. p. h., drawbar h. p. per ton car weight pulled = 0.597. Drawbar h. p. necessary to generate 1 kw. power at car axle is constant, regardless of train speed, and equals 1.86. Therefore (1.86/0.597) = 3.11 tons equivalent weight.

Figure 1 shows the power-plant load balance for a 6-ton compressor system using a 15-kilowatt, 38-volt, direct current, gear-driven, axle generator as its power supply in conjunction with the 1000 ampere-hour storage battery, and assumes it is in service on an actually existing 24-hour train between New York and Chicago. The time factors are taken from the actual time-speed curves for this particular train. Although the run is only 24 hours, the load maximum is taken to be 25 hours to include one hour of precooling, a half-hour of lighting before the train departure, and a half-hour of lighting after arrival at its destination. As the train speed is such that the generator car carries the load only 19 hours, the battery must carry the load the remaining 5 hours.

The power consumption may be as high as 8790 ampere hours, but throughout the entire trip the generator can produce only 7125 ampere hours. The difference is 1665 ampere hours, or 665 ampere hours greater than the reserve current in the storage battery. On this run, which is far more favorable than the average, the battery would frequently arrive at the terminal in a badly discharged condition; under severe conditions the power plant would fail entirely before arrival. To recharge the battery would require 1111 ampere hours, assuming the battery to have a 90 per cent efficiency as it had when new. During this run under severe conditions, the battery, although of only 1000 ampere-hour capacity, would be called upon to furnish 2282 ampere hours of current, or at the rate of 2.282 cycles of battery operation per day. Under such conditions, a battery cannot be expected to give anywhere near its normal life.

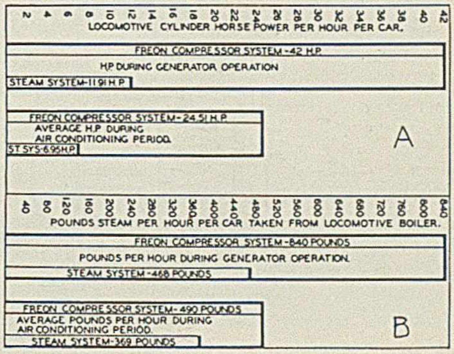


Figure 4. Relative Power Requirements from Locomotive

A. Freon compressor system
B. Steam ejector system

Figure 2 is a chart showing the power-plant load balance for a steam ejector system of air-conditioning (to be described in detail later) for exactly the same run and using exactly the same factors for lamp load and time. In the 19 hours available, the 9 kilowatts of generator capacity will produce 4275 ampere hours as against 2937 ampere hours taken by the load. In this case the battery is figured at 1000 ampere hours, although on the run it would only be called upon to furnish 731 ampere hours, or less than one cycle of operation in 24 hours. Actually a 600 ampere-hour battery would be ample in this case. Although 1338 ampere hours of surplus generator current are available, the methods of generator regulation used cause a reduction in the generator output to practically zero if there is no demand for the current.

It has been shown that a 15-kilowatt generator is hardly large enough for a 6-ton, electrically driven, compressor system. It might be argued that a generator even larger than 15 kilowatts capacity could be used. Figure 3 is a curve which has been plotted from data obtained from the motive power engineering department of one of our large railroads, and checked by the mechanical engineering department of another, to show the drawbar horsepower necessary to produce a kilowatt of electrical current from a car axle and the added tonnage per car which could be hauled at various speeds for the expenditure of the same power. The drawbar horsepower per kilowatt is 1.86 constant, regardless of speed. This is sufficient to move 7.7 additional tons of car weight at 20 miles per hour. For a 15-kilowatt generator the power would be sufficient to move 115.5 extra tons of weight at 20 miles per hour. Twenty miles per hour is approximately the train speed at which the generator delivers its full load. A standard Pullman car weighs 80 tons. To operate a 15-kilowatt generator from the car axle at 20 miles per hour is equivalent to increasing the car weight by 145 per cent. If all the cars on a train are equipped, it means more than doubling the effective train weight. At 60 miles per hour the situation is not so serious. Under this condition the equivalent added weight becomes 22.5 tons per car or 28 per cent per car, or per train as the case may be.

The difference in steam consumption is of no particular importance, but the additional mechanical horsepower required by the locomotive cylinder is of great importance, especially if applied to all cars of a fourteen- or fifteen-car train, and would vitally affect the locomotive performance. On a 15-car train, the steam ejector would save 451 horsepower.

It was such considerations as these which caused this company definitely to abandon hope of producing an adequate compressor type of system if the power was to be taken from the car axle.

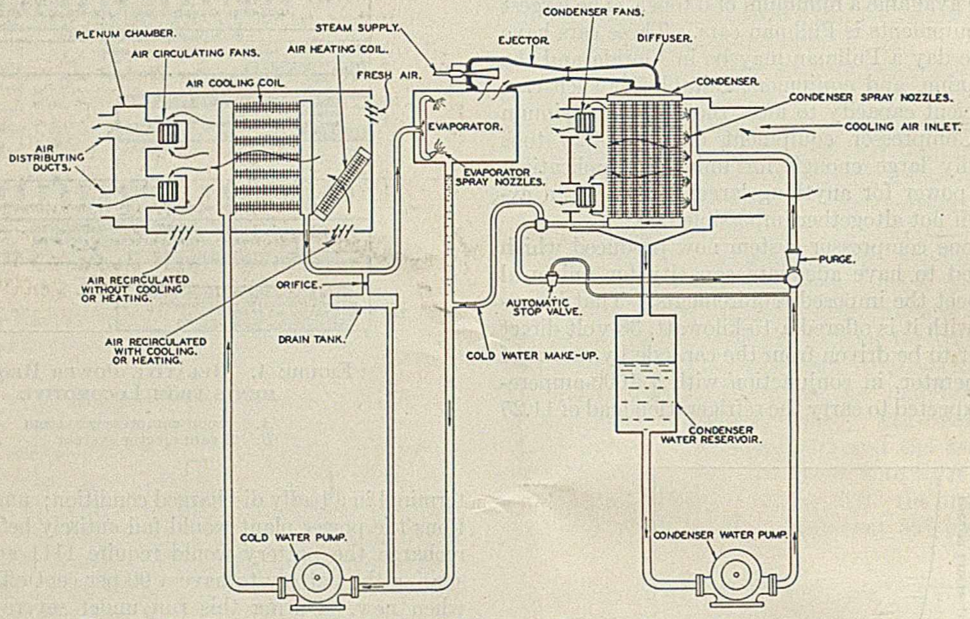


FIGURE 5. SCHEMATIC DIAGRAM OF CARRIER SAFETY STEAM EJECTOR SYSTEM

Figure 4 shows the relative power requirements from the locomotive for a 6-ton Freon compressor system *vs.* a 6-ton steam ejector system. For the purpose of developing the relation, a 10-hour train run was chosen during which the generator was at or above its full load speed for 7 hours. With a 2-hour precooling period, the battery load would be 5 hours. For both systems the time has been taken exactly the same and considers only the air-conditioning load; the lighting load is neglected entirely.

For the compressor system electrically driven, the locomotive cylinders have to develop 42 horsepower per hour per car while the generator is in use. For the steam ejector system, they have to develop but 11.91 cylinder horsepower while the generator is in use. For the average over the 12-hour period during which the air-conditioning load is on, the locomotive cylinder horsepower for the compressor system is 24.51 per hour per car; the average locomotive cylinder horsepower for the steam ejector requirements is 6.95 per hour per car.

Based upon the commonly accepted conversion value of 20 pounds of steam per indicated cylinder horsepower, the compressor system requires 840 pounds of steam per hour per car while the generator is in use. The steam ejector system requires 238 pounds per hour per car for the electrical input and 200 pounds per hour per car for the ejector; figuring 30 pounds per hour per car for train line condensation, a total of 468 pounds per hour per car is required while the generator is in use. For the average over the 12-hour period during which the air-conditioning load is on, the compressor system requires 490 pounds of steam per hour per car, and the steam ejector 369 pounds.

STEAM EJECTOR SYSTEMS

The principle of cooling a body of water in a container open to the action of a steam jet has long been known. In stationary work it probably is not as efficient as a mechanical system where ample electric power is available, but such a system has no difficulty in competing with electrically or mechanically driven equipment on a car where the power must be made and stored as it goes along. Under these conditions the steam ejector system is in a class by itself.

On a railroad train we have an ample supply of steam direct from the locomotive boiler through the train line. In 1930 the Carrier Engineering Company developed a system of air-conditioning for railway passenger cars, utilizing the steam itself to secure the refrigeration effect and limiting the use of electric power to that required to drive four fractional horsepower motors for two water pumps and two blower fans. Nothing is used in this system other than steam, water, and electric current, and the capacity can be anything wanted within reason. From 4 to 7 tons are available merely by changing the size of the ejector nozzle. The ejector steam consumption is changed from 135 to 235 pounds per hour through this same capacity range. There are twenty-six systems of 6-ton capacity in daily service. They have functioned through the entire summer in a satisfactory manner and with small operating expense.

The law upon which the steam-ejector refrigeration principle is based has been known for many years. It is, briefly, that water, or any other fluid used as a refrigerant, will assume a temperature corresponding to the pressure of the region within which it is contained. The lower the pressure is maintained, the lower will be the temperature. Thus, if a low pressure is maintained by means of a steam ejector nozzle within a region we shall call an evaporator, and if water which is circulated through this region enters at a temperature higher than that corresponding to the pressure maintained therein, it will evaporate rapidly to leave at a temperature corresponding to that pressure. The low pressure is constantly maintained because the steam ejector removes the water vapor as rapidly as it is formed at a definite point of equilibrium.

To attain a 40° F. water temperature leaving the evaporator, the absolute pressure within the evaporator must be maintained at 0.23 inch of mercury. This will be a 29.69-inch vacuum corresponding to a 29.92 barometer reading. The water passing through the evaporator is in constant circulation between the evaporator and the coils of the air-conditioning unit where it receives heat from the air. This newly acquired heat in the water is then given up by the latent heat of vaporization when it returns to the evaporator. It is a continuous cycle. The water is cooled in the evaporator, warmed in the air-conditioning unit, cooled again in the evaporator, etc.

Figure 5 is a schematic diagram of the steam ejector system. Live steam from the train line first passes through a reducing valve and a separator to remove the remaining moisture; then it passes through an automatic steam valve to the point marked "steam supply," where it enters the nozzle. In passing through this nozzle, the steam expands down to a low pressure and leaves at a high velocity. As the tip of the nozzle is at a low pressure, the water vapor in the evaporator will flow toward this, and will, therefore, be entrained and carried away by the high-velocity steam jet. In order to operate economically, the steam and entrained water vapor are condensed, but to do this at the condensing conditions met, the pressure of the steam and entrained water vapor is raised by utilizing a reverse nozzle. After the steam leaves the reverse nozzle it passes through the diffuser to enter the condenser. In this, heat removal is brought about by the fact that outside air, which is drawn over the condenser tubes by means of the condenser fans, evaporates a portion of the condenser water which is sprayed over the outside surface of the condenser tubes. The saturated air is discharged immediately by the fans.

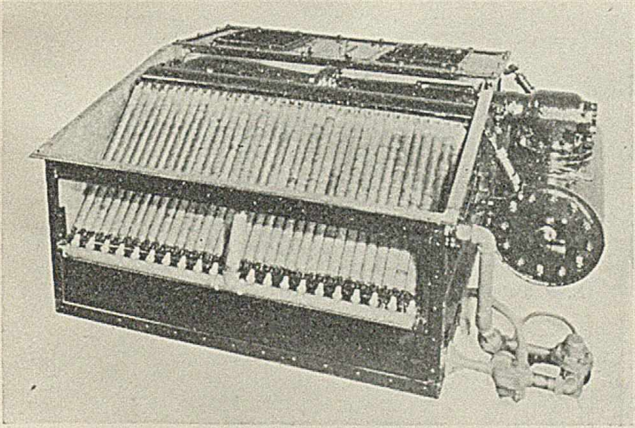


FIGURE 6. REAR VIEW OF REFRIGERATION UNIT WITH COVERS REMOVED

Figure 5 shows that the cold water cycle is continuous between the cooling coils and the evaporator. In this unit, the water receives heat from the air, which is later given up in the evaporator. The air delivered to the car by the fans is obtained from two sources—namely, a definite portion of outside air to maintain good ventilation, and a definite portion of return air from the car which is essentially at the car temperature being maintained. This return air may either pass over the coils to be lowered in temperature, or a portion or all of it may by-pass the coils, the quantity depending entirely upon the temperature requirements at the car. The by-pass and return air dampers are automatically controlled by means of the car thermostat.

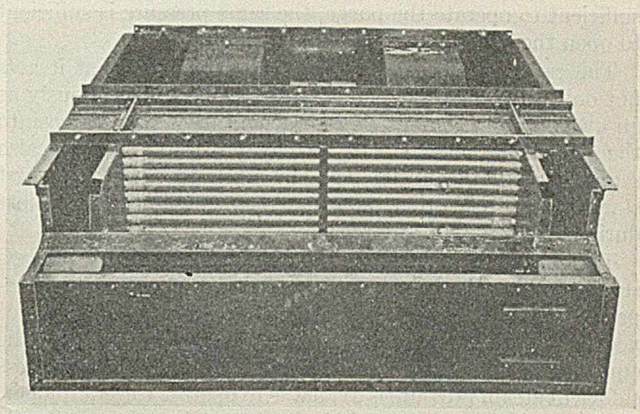


FIGURE 7. REAR VIEW OF AIR-CONDITIONING UNIT WITH COVERS REMOVED

As the air-conditioning system is for year-round operation, precaution must be taken to prevent the cold incoming outside air from freezing the water in the cooling coils of the air-conditioning unit during periods of low outside temperatures. To prevent this, a drain tank is placed below the coils, and it fills to allow the water level to recede below the level of the air-conditioning unit upon shutdown of the system. By proportioning the orifice entry in the tank to the sizes of the main water-circulating pipes, only an insignificant quantity of water enters the tank during operation and drains out continually to the pump suction to keep the tank empty during operation.

Close to 3.3 pounds of steam per minute passes through the nozzle (Figure 5) to evaporate, for example, 1.12 pounds of water per minute. Thus 4.42 pounds of steam per minute must be condensed in the condenser. To do this, at least 4.42 pounds of condenser water must be evaporated from the surface of the condenser tubing, eliminating any possible air condensing. At first glance this 4.42 pounds appears to be lost from the condenser water tank beneath the car, but this is not wholly the fact.

It was previously stated that around 1.12 pounds of water per minute are evaporated from the cold water side per minute, and, obviously, this must be replenished; otherwise the cold side would soon become depleted of water. This replenishing is done without the use of float valves by utilizing the difference in pressure between the evaporator and the condenser, and thus the make-up comes over from the condenser. This then takes care of 1.12 pounds of the total condensed in the condenser. As seen, the cold water make-up has first choice of the condensate, and only that which is needed is taken. The remaining condensate is taken out by a water jet evacuator, or purge, which handles all the condenser water circulated by the pump. As this condenser water with the entrained condensate is sprayed over the condenser coils, and, after undergoing a slight loss in quantity by evaporation, returns to the make-up tank, it is seen that although 4.42 pounds of water are evaporated in the cooling condensing tower, 3.2 pounds are received in the form of condensate and thus only 1.12 pounds per minute are actually lost from the system. At the beginning of a refrigeration period the make-up tank is filled to the maximum level, but the level recedes constantly as water is lost. At various servicing points along the road, the make-up tank is refilled.

In order that, after a period of shutdown, refrigeration may be resumed quickly, a check valve is installed between the condenser and the purge. When the system is shut down and the pressure from the condenser pump is off, this check valve closes and holds the vacuum. Upon starting the system, as soon as the water pressure from the condenser pump is sufficient to operate the purge, the same pressure is sufficient to open the check valve.

The capacity of the purge is large enough so that it acts not only to remove the condensate, but also continuously as an evacuator to remove any air which may have come into the system with the steam, or any possible leaks. It also serves to pull the initial vacuum when the system is first started, or at any other time should the vacuum become lost during shutdown for any reason.

The controls are simple and consist chiefly of a steam pressure switch, a condenser pressure switch, an automatic temperature shut-off switch for the refrigeration when it is not needed, and two manual electric starting buttons for the equipment. The steam pressure switch does not close unless sufficient steam pressure is available to operate the equipment. The condenser pressure switch does not allow the automatic steam valve to open until a sufficient vacuum has been pulled by the water jet in case the vacuum has been lost. In the event the system has been started, and the conditions finally become such that no more cooling is needed, the return air dampers will close completely and at that point will open a switch to cut off the refrigeration. The starting buttons operate the relays for the four motors used.

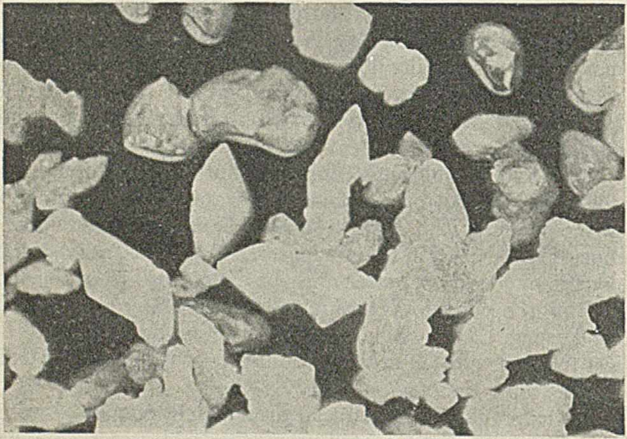
Figure 6 is a view of the refrigeration unit and shows the evaporator, ejector casting, condenser tubing, condenser water spray headers, cold water make-up connection, pressure check valve, water jet evacuator, and fan discharge openings.

Figure 7 is a view of the air-conditioning unit and shows the automatic temperature-control damper frame, cooling coils, by-pass air space, and circulating fans. The heating coil is not visible.

A schematic view of a steam ejector system on a railroad car is shown in the illustration appearing at the beginning of this article. The refrigeration unit is at the top left-hand side, and the air conditioning unit at the top right-hand side. The air inlets to the car are in the side deck. Below the car the condenser water pump and make-up tank are shown in the center. The cold water pump is shown beneath the car at the extreme right. The vertical cylindrical tank in the cold water circuit serves its purpose to increase the volume of cold water in order that a period of uniform cooling may be effected without refrigeration, as would be the case when the locomotive is removed for change at division points. It has been found, however, that the additional quantity is not necessary, and the use of the tank has been discontinued.

At present, a steam ejector system is also offered which places the refrigeration unit beneath the car, and the air-conditioning unit vertically inside the car. This obviates any roof changes.

Received November 8, 1932.



Left: Potassium Perrhenate Crystals (× 8) Containing About 65 Per Cent Rhenium

The rhenium metal and the potassium perrhenate shown in these two pictures (see text, page 7) are of commercial quality as manufactured by the Vereinigte Chemische Fabriken zu Leopoldshall, Germany (represented in this country by Gerhard Wagner, 25 Broadway, New York, N. Y.). Photographs by E. P. Polushkin, Columbia University, New York.

Right: Rhenium Metal Powder (× 200)

The metal is almost in colloidal form, and each particle is smaller than one micron. It was extremely hard to obtain a picture showing these particles which are difficult to separate from each other; however, in several spots in the picture they can be easily distinguished. The manufacturer guarantees a purity of the material in this form of 99.5 per cent (impurities, potassium and silica).

Symposium on Priming and Finishing of Nonferrous Surfaces

Presented before the Division of Paint and Varnish Chemistry at the 84th Meeting of the American Chemical Society, Denver, Colo., August 22 to 26, 1932.

Aircraft Finishing

M. R. Whitmore, U. S. Army Air Corps, Dayton, Ohio

The framework and surfaces of Army aircraft are painted to obtain a characteristic color scheme and as a protection against corrosion which may cause tremendous changes in the physical properties of the metals.

The available protective coatings may be divided into three groups: organic coatings (paints, lacquers, greases), metallic coatings (electrodeposits, galvanizing, etc.), and chemical or electrochemical treatments (anodic treatment, Parkerizing, etc.). Each type is used by the Air Corps, and in practically all cases a paint coating is applied to the metal, previously treated by one of the other methods. Practically all steel, brass, and bronze parts and surfaces are cadmium plated, and all aluminum and aluminum alloy parts are anodically treated.

Corrosion and vibration tests show that paint coatings for aircraft should possess, besides durability, the following characteristics: high resistance to permeability by water, pigments which will tend to passivate metals and prevent corrosion, absence of pigments of alkaline reaction, good adhesion to metal which may not be chemically clean, and high resistance to impact and bending even after exposure.

THE framework and surfaces of Army aircraft are painted for two reasons: to obtain a characteristic color scheme, and what is of far more importance, as a protection against corrosion. They are not painted merely because the red rust of iron or the white rust of aluminum are particularly unsightly, but rather because the tremendous changes in the physical properties of the metals occasioned by this rust make protective coatings for aircraft imperative. Airplanes must be strong, rigid, and light. These requirements necessitate the employment of light strong alloys and an extensive use of thin-gage material in their manufacture.

Recently, the metal wing covering of an airplane was examined which had been in service from February, 1928, to January, 1932. The airplane had been stationed at Dayton, Ohio, and Rantoul, Ill., for the entire 4 years. This midwestern area represents mild conditions from the standpoint of corrosion. The wing covering was corrugated heat-treated aluminum alloy (duralumin), the interior (unexposed) surface of which was coated with spar varnish at manufacture, whereas the exterior had no protective coating of any kind. This metal covering originally had an ultimate strength of 60,000 to 65,000 pounds per square inch (4218 to 4570 kg. per sq. cm.) and an elongation in 2 inches (5 cm.) of 18 per cent. Table I gives the physical properties obtained on specimens cut from the metal covering and shows clearly the deterioration, especially as regards elongation, after 4 years of service under extremely mild conditions.

Surface corrosion of the wing covering was barely noticeable, and under magnification the corroded areas were minute. Nevertheless, it was sufficient on this thin-gage metal to reduce the physical properties to a marked degree. Unfortunately, the condition is aggravated in this type of alloy, as the corrosion is not so much the surface or pitting type, but one that proceeds along the grain boundaries (intergranular corrosion) and destroys the strength of the metal with little or no surface evidence.

When corrosion can progress to this extent under mild conditions of service, it is apparent that protective coverings must be employed when most of the airplanes are operating in tropical and coastal areas where high humidity and salt water are always present.

Table I. Physical Properties of Metal Wing Covering after 4 Years

Thickness of Metal	Location of Specimen	Ultimate Strength	Elongation
Inch		*Lb./sq. in.* *(kg./sq. cm.)*	*% in 2 inches*
0.010	Bottom of wing	53,000 (3726)	6.5
0.010	Bottom of wing	50,000 (3515)	5.5
0.010	Bottom of wing	46,000 (3234)	6.0
0.010	Bottom of wing	50,000 (3515)	...
0.010	Bottom of wing	38,000 (2671)	3.3
0.013	Top of wing	52,000 (3656)	6.0
0.013	Top of wing	47,000 (3304)	2.0
0.013	Top of wing	50,000 (3515)	3.5
0.013	Top of wing	52,000 (3656)	5.0
0.013	Top of wing	55,000 (3867)	5.5
0.020	Top of wing	58,000 (4077)	12.0
0.020	Top of wing	57,000 (4007)	8.5
0.020	Top of wing	55,000 (3867)	8.0
0.020	Top of wing	57,000 (4007)	8.0

Protection against Permeability by Water

The available protective coatings may be divided into three groups: organic coatings (paints, lacquers, greases), metallic coatings (electrodeposits, galvanizing etc.), and chemical or electrochemical treatments (anodic treatment, Parkerizing, etc.). Each type is used by the Air Corps, and in practically all cases a paint coating is applied to the metal previously treated by one of the other methods. Practically all steel, brass, and bronze parts and surfaces are cadmium plated, and all aluminum and aluminum alloy parts are anodically treated.

This treatment (usually termed "anodic treatment") consists in making the aluminum part the anode in a 3 per cent solution of chromic acid at a temperature of 40° C. The voltage across the bath (the iron tank is made the cathode) is gradually raised from 0 to 40 volts in 15 minutes. This potential is maintained for 35 minutes when the voltage is gradually increased to 50 in 5 minutes and held at that voltage for 5 minutes. This treatment places a hard, adherent, glassy coating of aluminum oxide on the metal. The coating is a nonconductor of electricity, has a thickness of about 0.75 micron (3×10^{-5} inches), and absorbs approximately 0.041 gram (*1*) of chromic acid per square meter. The coating offers considerable protection in itself against corrosion and has the added feature of making an excellent base for paint materials both from the standpoint of adhesion and corrosion resistance. A paint coating over anodized aluminum alloy will withstand about five times as long an exposure to salt water as the same coating over untreated metal. Table II gives a few of the results obtained by using various metal primers over treated and untreated duralumin sheet. The sulfuric acid anodic treatment consisted in making the panel the anode in 15 per cent by volume solution of sulfuric acid. Sheet lead was used as the cathode. The treatment was for 30 minutes with the solution maintained at 25° C. The voltage across the bath was held constant at 12, and the average current density was 8.6 amperes per square foot (0.93 amperes per sq. dm.). An alkaline chromate solution was used for the immersion process. The time of treatment was 5 minutes, and temperature of the solution 95° C.

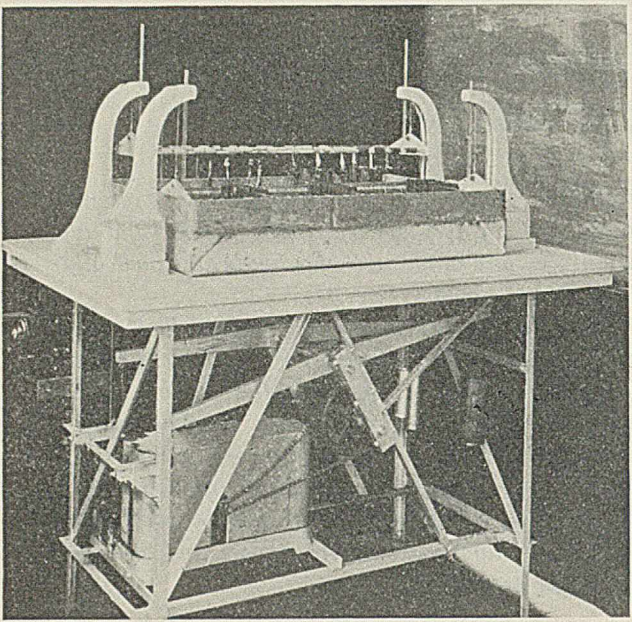


FIGURE 1. APPARATUS FOR INTERMITTENT IMMERSION OF TEST PANELS

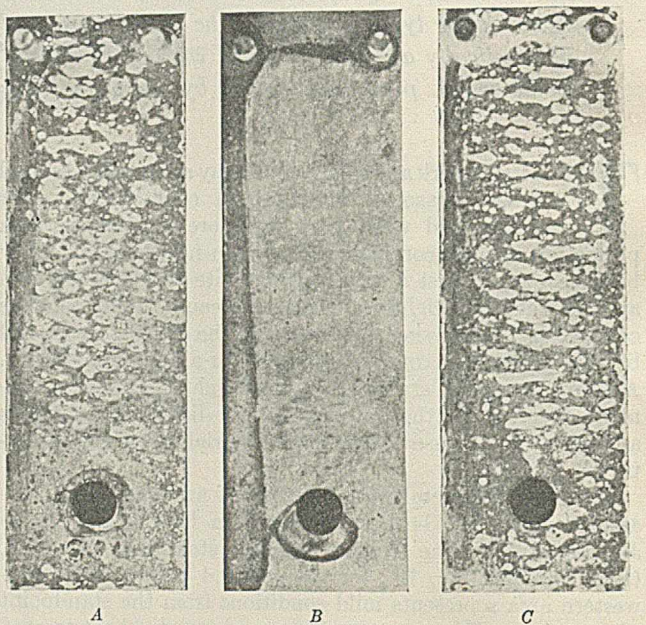
Primers 1, 2, and 3 (Table II) were products which had previously been tested and showed poor, fair, and good resistance, respectively, to salt water exposure. The finish in all cases consisted of two light spray coats of primer. The exposure was made by subjecting the panels to intermittent immersion in a 20 per cent by weight solution of sodium chloride. The apparatus used is shown in Figure 1. With this machine the specimens are immersed in the salt water for one minute and then raised out of the solution and allowed to air-dry for 15 minutes before the next immersion. The machine operates automatically and continuously. Hard rubber tanks are used as containers for the salt solution.

TABLE II. DURABILITY OF PRIMERS IN SALT WATER OVER TREATED AND UNTREATED METAL

PRIMER	BASE	TREATMENT	EXPOSURE *Weeks*	CONDITION[a]
1	Oil	None	1	C
2	Oil	None	7	C
3	Oil	None	7	B
1	Oil	CrO_3 anodic	6	C
2	Oil	CrO_3 anodic	29	B
3	Oil	CrO_3, anodic	29	B
1	Oil	15% H_2SO_4, anodic	2	C
2	Oil	15% H_2SO_4, anodic	29	C
3	Oil	15% H_2SO_4, anodic	29	B
1	Oil	Immersion process	2	C
2	Oil	Immersion process	10	C
3	Oil	Immersion process	20	B
7	Pyroxylin	None	7	C
7	Pyroxylin	CrO_3, anodic	29	C
12	Pyroxylin	None	6	C
12	Pyroxylin	CrO_3, anodic	29	A
15	Synthetic	None	3	C
15	Synthetic	CrO_3, anodic	14	A
16	Synthetic	None	4	C
16	Synthetic	CrO_3, anodic	14	C

[a] A, good; B, fair; C, failure.

As previously stated, steel, brass, and bronze parts are cadmium plated as the initial protective coating. Cadmium offers several desirable features as a protective coating for aircraft parts. It has excellent resistance to salt water; only a thin (0.0003 to 0.0005 inch, or 0.0008 to 0.0013 cm.) coating is necessary for satisfactory protection as compared to 0.0015 to 0.0025 inch (0.0038 to 0.0064 cm.) for equivalent protection by zinc; it is electronegative to the aluminum alloys in salt water, which is desirable where dissimilar metals come in contact with aluminum. Its one bad characteristic is the difficulty in obtaining satisfactory adhesion of paint coatings to the metal. This point will be discussed later.



A B C

FIGURE 2. TEST PANELS AFTER 10-DAY INTERMITTENT EXPOSURE TO SALT WATER

A. Heat-treated duralumin
B. Cadmium-plated steel (cadmium, 0.0012 inch)
C. Tinned steel

DISSIMILAR METAL CONTACT

Dissimilar metal contact is important in aircraft construction from the standpoint of corrosion, and suitable insulation of the parts is necessary. Aluminum, being high in the electromotive series, is the corroding metal in most couples; because of its susceptibility to both the pitting and intergranular type of corrosion, the metal is soon weakened. The rate of corrosion in any dissimilar metal cell is governed, among other factors, by the potential developed.

A series of tests was recently made to determine the susceptibility to corrosion of duralumin in contact with the various metals used in aircraft construction and also the polarity and potential developed by the various metal-duralumin couples. The corrosion test panels were prepared by inserting two rivets for each of the metals tested in a 1 × 6 × 0.020 inch (2.5 × 15.3 × 0.05 cm.) heat-treated duralumin test specimen and subjecting the panels to intermittent immersion in a 20 per cent sodium chloride solution for 10 days. The physical properties of the aluminum alloy sheet after the 10-day exposure to salt water are given in Table III. Each value is the average of four test specimens. The original properties of this sheet were: ultimate strength, 60,000 pounds per square inch (4218 kg. per sq. cm.); elongation, 18 per cent in 2 inches (5 cm.).

TABLE III. PHYSICAL PROPERTIES OF DURALUMIN SHEET IN CONTACT WITH VARIOUS METALS AFTER 10-DAY EXPOSURE TO SALT WATER

METAL RIVETS	ULTIMATE STRENGTH *Lb./sq. in. (kg./sq. cm.)*	ELONGATION *% in 2 inches*
Aluminum	44,900 (3156)	5.0
Annealed duralumin	46.400 (3262)	5.6
Heat-treated duralumin	36,840 (2590)	3.4
18–8 steel	38,700 (2721)	3.25
Copper	31,600 (2221)	2.1
Brass	29,950 (2105)	1.6
Low-carbon steel (1020)	32,250 (2267)	2.4
Tinned steel	36,290 (2551)	3.1
Cadmium-plated steel	55,800 (3923)	16.1

For the potential measurements each cell contained 200 ml. of salt solution in a 400-ml. Pyrex beaker, and sheet electrodes (one of which was always heat-treated duralumin) 5 × 0.5 inch (12.7 × 1.3 cm.). The polarity of the electrodes was determined by the polarity of the standard cell terminal opposed to each electrode. The potentials were determined by means of a potentiometer and galvanometer on open circuit after the cell had been closed for 16 and 64 hours. The values are shown in Table IV.

It will be noted from the potential measurements that cadmium and aluminum are the only metals included in this test which offer electrolytic protection to duralumin in dissimilar metal couples when the electrolyte is sodium chloride. Zinc was not included in the test because very little zinc is employed in aircraft construction. The metal, however, is anodic to aluminum and its alloys in sodium chloride as shown by Edwards and Taylor (2). The practical side of these measurements is borne out in the corrosion test panels of Table III and is quite striking in the case of cadmium. Although cadmium is electronegative to duralumin to the same degree as aluminum, the protection offered by the former was much greater in the test. Figure 2 shows a photograph of panels containing duralumin, tinned steel, and cadmium-plated rivets after the 10-day exposure to salt water. Photomicrographs taken of the specimens showed that the specimens with cadmium-plated rivets were the only ones in which intergranular corrosion was not evident.

TABLE IV. POTENTIAL MEASUREMENTS OF VARIOUS METAL COUPLES

(In volts)

		POTENTIAL MEASUREMENT			
		Electrolyte, 1 *N* NaCl		Electrolyte, 3.5 *N* (20%) NaCl	
COUPLE	ANODE OF CELL	16 Hours	64 Hours	16 Hours	64 Hours
Duralumin,[a] aluminum	Aluminum	0.16	0.16	0.21	0.16
Duralumin, copper	Duralumin	0.40	0.41	0.33	0.37
Duralumin, brass	Duralumin	0.48	0.43	0.35	0.38
Duralumin, annealed duralumin	Annealed duralumin	0.08	0.10	0.08	0.11
Duralumin, 18–8 steel[b]	Duralumin	0.38	0.38	0.33	0.33
Duralumin, low-carbon steel	Duralumin	0.04	0.04	0.04	0.04
Duralumin, tinned steel	Duralumin	0.08	0.08	0.08	0.10
Duralumin, cadmium-plated steel	Cadmium	0.15	0.10	0.18	0.15
Duralumin, duralumin[a]	......	0.0	0.0	0.0	0.0
Duralumin, zinc	Zinc	0.48[c]	..	..	..

[a] Heat-treated condition.
[b] 18% chromium, 8% nickel.
[c] Value reported by Edwards and Taylor (2).

These remarks on corrosion are made to bring out the importance and necessity of protective coatings for aircraft. Paint coatings are effective only so long as the film is intact and in the degree to which they prevent access of water to the metal. Once the film is broken or allows water to penetrate to the metal, the film probably locally accelerates rather than retards corrosion, owing to the formation of oxygen concentration cells. A possible exception may be made in some instances for coatings containing chromates or other passivating pigments. It is because of the rather uncertain protection which a paint coating may offer that initial coatings, such as cadmium plating, anodic treatment, insulation of metal couples with bitumastic paint, or other waterproofing compounds are employed, before the application of metal primer and enamel. Oil-base metal primer and oleoresinous enamels have been standardized as the finish coats for Army aircraft, not because they necessarily offer greater durability or water resistance but because they have proved far superior to other finishing schemes from the standpoint of adhesion. All attempts to use pyroxylin finishing systems have been unsatisfactory because of premature peeling, chipping, and cracking. In many cases this could be traced to application of the finish on unclean metal. The necessity of protecting both interior (unexposed) and exterior surfaces requires the assembly of many partly painted structures, and the surfaces after assembly are often none too clean. The task of cleaning a large all-metal wing, for example, for a lacquer finish can be appreciated.

PREVENTION OF ALKALINITY

Evans (3) has offered the "alkaline peeling" theory by which paint failures may be attributed to alkali developed during corrosion of the metal. That a high degree of alkalinity will develop instantly on certain metals when wet with neutral water and without any visible evidence of corrosion may not be generally known. It is easily demonstrated if pieces of steel, cadmium, aluminum, and magnesium, for example, are cleaned to remove scale and to produce a chemically clean surface, and are rinsed thoroughly in neutral water, and if the adhering water film is spotted with phenolphthalein indicator. A pink color will develop immediately on the cadmium and magnesium (much stronger on the latter) but not, even after standing several minutes, on the steel and aluminum. Since the pH range of phenolphthalein is 8.6 to 10.2, a pH of more than 9.0 is indicated by this test.

During a corrosion test on magnesium sheet, it was noticed that the pH of 30 liters of a 20 per cent sodium chloride solution changed from 6.9 to 9.6 in 10 days. Approximately 100 square inches of the metal were exposed to the solution. The intermittent machine was used for the test so that the metal was actually in the solution only 96 minutes in every 24 hours. This led to the investigation of the change in pH of neutral solution due to the presence of various metals.

Test specimens approximately 0.75 inch (1.91 cm.) wide and 5 inches (12.7 cm.) long of the metals used in aircraft construction were employed. One specimen of each metal was placed in one of three 300-ml. Erlenmeyer flasks containing boiled distilled water, 1 *N* (6 per cent) and 3.5 *N* (20 per cent) sodium chloride, respectively. The salt solutions were made up with boiled distilled water. The flasks were covered with watch glasses and placed in a room free from laboratory fumes. Blank solutions were run to correct for any changes due to contact with the glass or absorption of gases. The pH of each solution at 25° C. was determined on a Hellige comparator after various exposure periods.

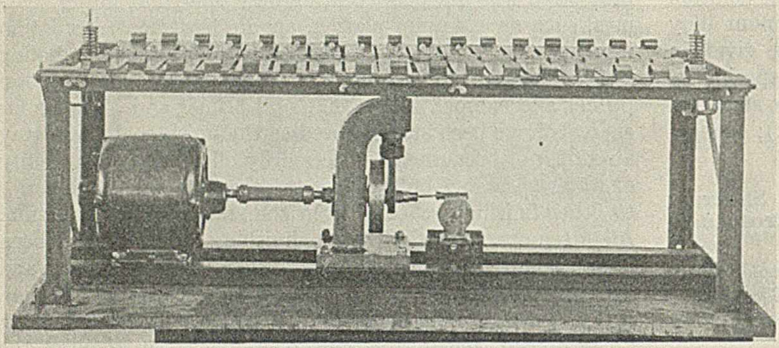


FIGURE 3. SIDE VIEW OF MACHINE FOR VIBRATION TESTS

The results are given in Table V. The values reported are in most cases the average obtained with two indicators. In the case of copper and brass satisfactory color matches could not be obtained, probably because of salt effect on the indicators, and the values for those metals may be in error. It is evident from Table V that a high degree of alkalinity is developed during the corrosion of magnesium, cadmium, and zinc. This, together with the fact that a pH of about 9.0 develops instantly when cadmium and magnesium are wet with water, may explain in part the difficulty of obtaining satisfactory paint coatings on these metals.

The pH values reported are those obtained under conditions which allow free access of oxygen from the air and where the more stable hydroxides or hydrated oxides will form. Where free access of oxygen is not available, as under a paint film, unstable hydroxides may form, and the degree of alkalinity may be quite different. This is known to be true for iron and is quite possible with some of the other metals. Steel panels, especially when coated with a pyroxylin primer, will often show a marked tendency after exposure to salt water for the entire film to peel or slide off the metal. Underneath the paint coating, green ferrous hydroxide is quite evident. The pH of a saturated solution of this hydroxide is 9.5, compared to about 7.0 for the more stable ferric compound which is formed where free access of oxygen is available. Since pH is a logarithmic function, the degree of alkalinity of the ferrous hydroxide is 315 times that of the ferric compound.

Any means, therefore, by which the solution of the metal may be prevented or even retarded and which will thus prevent or retard the formation of an alkaline film at the paint-metal interface by the presence of water, will increase the life and durability of paint films under corrosion conditions. This has been accomplished in the case of cadmium by passivating the metal in chromic acid. It was the general opinion that the failure of paint films on cadmium-plated parts was caused by traces of alkali remaining on the metal from the cyanide plating bath. As stated previously, the water film on clean cadmium will turn phenolphthalein immediately. If the plate is dipped in dilute sulfuric acid, which would neutralize any surface alkalinity, and then rinsed acid-free with water and spotted with the indicator, the pink color will develop after a few seconds. However, if the plate is dipped in chromic acid (3 to 10 per cent), rinsed, and spotted, the indicator will not turn pink even after standing until the water has evaporated. This change, caused by the acid dips, is not one of neutralization of surface alkali, but rather the formation of superficial coatings of insoluble sulfates and oxides, respectively, the latter of which is much more effective. That the cadmium is really passivated is shown by the fact that, whereas cadmium deposits may be readily stripped from steel or brass by immersion in a 10 per cent solution of ammonium nitrate, a plate which has been dipped in chromic acid cannot be removed by this method. This treatment has proved successful in actual service. One company to whom the method was recommended reported: "A sufficient number of production parts have now been processed by this method to indicate that it has successfully overcome our difficulties and will be used on all future production."

FLEXIBILITY AND RESISTANCE TO CHIPPING

Another important requirement of airplane finishes is flexibility and resistance to chipping under impact. It is important both from the standpoint of appearance and corrosion. It has often been stated that the cracking of finishes has been caused by vibration at the low temperature encountered at high altitudes. With one or two oil enamels it was found possible to crack and check the film by chilling the panel from room temperature to −40° C. in about one minute with carbon dioxide snow, but, in general, no failure occurred. All airplanes vibrate to a greater or lesser extent, and the effect of this vibration or alternate bending on paint film was investigated. Zand (*4*) has shown that, regardless of the engine or propeller used, the frequency of vibration as measured at the instrument board is always equal to the engine speed. The amplitude of vibration as measured by the same author varied from 0.13 to 0.64 mm. on six different airplanes. He concluded that, for satisfactory performance of instruments, the amplitude should not exceed 0.25 mm. Paint coatings must withstand this bending, both when new and after exposure, at summer heat and at the low temperature (−20° to 60° C.) of high altitudes. The temperature

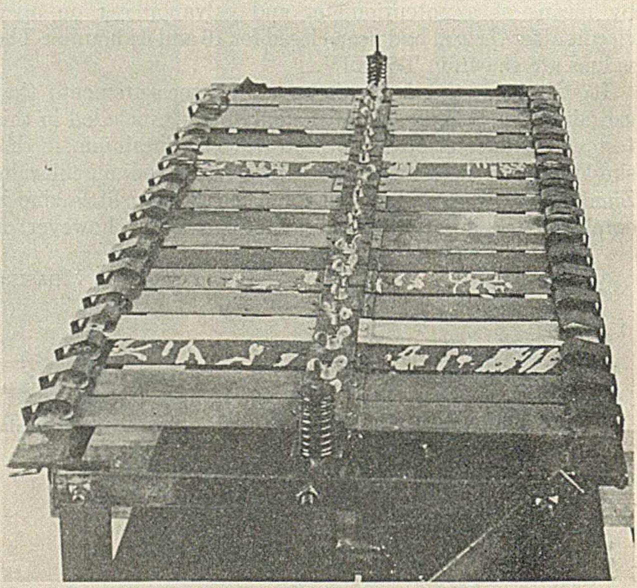


FIGURE 4. TOP VIEW OF MACHINE FOR VIBRATION TESTS

Table V. pH of Water Solutions in Contact with Various Metals

	Boiled Distilled Water					1 *N* (6%) NaCl					3.5 *N* (20%) NaCl				
Metal	0 Hour	24 Hours	48 Hours	96 Hours	400 Hours	0 Hour	24 Hours	48 Hours	96 Hours	400 Hours	0 Hour	24 Hours	48 Hours	96 Hours	400 Hours
Blank	6.7	6.7	6.8	...	6.9	6.7	6.8	6.8	..	7.0	6.6	6.6	6.7	..	7.0
Magnesium	...	9.7	9.9	9.9	9.9	...	11.7	12.0	12.4	12.4	...	11.6	11.6	12.0	12.2
Cadmium	...	7.4	8.5	8.3	7.8	...	9.6	9.4	9.6	8.8	...	9.7	10.0	9.4	9.4
Zinc	...	8.4	8.4	8.6	7.4	...	9.2	9.5	9.8	9.8	...	9.2	9.1	9.2	8.4
Iron	...	6.7	6.8	7.1	7.5	...	6.9	6.4	6.4	6.8	...	6.6	6.4	6.4	6.7
Aluminum	...	6.6	6.7	6.6	6.9	...	6.9	7.0	7.0	7.1	...	6.7	6.5	6.6	7.1
Duralumin	...	6.8	6.9	6.7	6.9	...	7.1	7.1	7.0	6.8	...	6.7	6.7	6.5	6.9
Nickel	...	7.1	6.9	7.1	7.3	...	8.9	8.8	8.8	8.8	...	8.8	8.9	8.8	8.8
Copper	...	6.7	6.7	6.7	6.7	...	7.2	7.1	7.1	8.8	...	8.8	8.6	8.6	8.7
Brass	...	6.8	6.8	6.8	7.2	...	8.1	7.8	8.1	8.2	...	8.8	8.8	8.7	8.7

change may also be quite rapid. A pursuit ship taking off with a ground temperature of 32° C. can climb to 20,000 feet in 15 minutes where the temperature will be about −18° C.

The machine used for the vibration test is shown in Figures 3 and 4. The frequency of vibration was 1750 and the amplitude of vibration 2.03 mm. (0.080 inch). It will be noted that this amplitude is eight times the maximum recommended by Zand. The panels were made of 0.040-inch (0.102-cm.) heat-treated aluminum alloy (duralumin) riveted together with a 2.5-inch (6.4-cm.) lap. The finishes consisted of auto lacquers, airplane dopes, oil enamels, and glycerol-phthalate enamels applied over two different oil-base primers. The coatings were applied by spray and then subjected to the following test procedure:

1. Baked for 24 hours at 100° C.
2. Vibrated 25 million cycles at room temperature.
3. Vibrated 7.5 million cycles at −40° C.
4. Exposed 60 days in Weatherometer.
5. Vibrated 20 million cycles at room temperature.
6. Vibrated 11 million cycles at −40° C.

Although none of the panels failed from alternate bending until the final vibration at low temperature (and only the most brittle finishes then), several of the finishes showed a marked tendency to chip under slight impact. The test did not simulate sudden temperature changes, nor were any panels included of thicker films such as would be used for highly polished finishes. Even though the results from the vibration test were rather negative, they did show that materials of satisfactory flexibility are not likely to fail from alternate bending due to vibration of the airplane, and that exposure to light and low temperature are conducive to failure.

Paint coatings for aircraft, therefore, should possess, besides durability, the following characteristics:

1. High resistance to permeability by water.
2. Pigments which will tend to passivate metals and prevent corrosion.
3. Absence of pigments of alkaline reaction. The failure of primer 1 of Table II is believed due in no small part to the large percentage of calcium carbonate used as an extender.
4. Good adhesion to metal which may not be chemically clean.
5. High resistance to impact and bending even after exposure.

Literature Cited

(1) Anonymous, "Anodic Oxidation of Aluminum and Its Alloys as Protection against Corrosion," Dept. Sci. and Ind. Research, His Majesty's Stationery Office, London, 1926.
(2) Edwards, J. D., and Taylor, C. S., *Trans. Am. Electrochem. Soc.*, 56, 27 (1929).
(3) Evans, U. R., *Ibid.*, 55, 243 (1929).
(4) Zand, S. J., *S. A. E. Journal*, 29, 263 (1931).

Received August 29, 1932.

Painting Aluminum

Junius D. Edwards and Robert I. Wray, Aluminum Research Laboratories, New Kensington, Pa.

THE painting of aluminum for decoration or protection presents much the same problems as the painting of other metals. However, because of the resistance of aluminum to atmospheric corrosion, painting has not generally been a necessity as in the cases of iron and steel. As a result little study had been devoted to the subject until the introduction of alloys, stronger but less corrosion resistant than commercially pure aluminum, made the study of protection imperative. This need arose particularly in the aircraft industry where lightweight sections heavily stressed must be assured against any deterioration. For most conditions of atmospheric exposure, no special technic is necessary in the painting of aluminum. For severely corrosive conditions, however, as against salt spray or intermittent immersion, investigation has developed special methods of surface preparation and types of paints which give greatly improved performance.

Before taking up the details of painting practice, something should be said about the varieties of aluminum and its alloys which may be presented for painting. Commercially pure aluminum—for example, 99 to 99.5 per cent in purity, is available in all common wrought forms as plates, sheet, tubing, extruded shapes, and rod and wire, and is designated as 2S. The wrought alloys are conveniently divided into two groups—the so-called common alloys and the strong alloys subject to heat treatment. The three best-known common alloys are 3S (an aluminum alloy with 1.25 per cent manganese), alloy 43S (containing 5 per cent silicon), and a more recent development, 4S (containing 1.25 per cent manganese and 1 per cent magnesium). The best known of the heat-treated alloys is duralumin or 17S, which contains 4 per cent copper, 0.5 per cent magnesium, and 0.5 per cent manganese. A special product with exceptional resistance to corrosion, sold under the trade-mark "Alclad," combines a central core of 17S with integral surface layers of high-purity aluminum. Another extensively used heat-treated alloy is 51S, having as alloying ingredients 1.0 per cent silicon and 0.6 per cent magnesium. This brief list does not cover all the commercially used wrought alloys of aluminum, but, since their painting characteristics are not appreciably different, it is sufficient for present purposes.

Aluminum alloy castings are sometimes painted, but mainly for purposes of decoration. Aluminum is commonly alloyed with copper, silicon, magnesium, manganese, nickel, and zinc. There are literally hundreds of aluminum casting alloys which are in use at one time or another where their special characteristics are demanded, either from the standpoint of foundry practice or service requirements. Here again there are no special differences noted with respect to their ability to take and hold paint, so that no detailed discussion of compositions is required.

Paint Adhesion

Generally speaking, aluminum and its alloys need paint protection only against severely corrosive conditions. In these cases the determining factor in paint protection is the adhesion between the metal and the paint coating and its degree of permanence. The most common cause for loss of paint adherence and blistering is the penetration of moisture through the paint coating and its reaction with the metal surface. There are, therefore, two factors involved: The more impermeable the paint coating, the less likelihood there is of moisture penetrating the coating in appreciable amounts; the second factor is the corrosion resistance of the aluminum surface or its passivity. Aluminum owes its corrosion resistance to the almost invisible film of oxide which it instantly acquires when exposed to moist air. The protective action of this film depends to some extent upon its thickness, but is also dependent on its continuity, which in turn is affected by the alloying constituents which may be present in the metal. When aluminum is oxidized by moist air, hydrogen is liberated; if this gas liberation occurs beneath a paint coating and at too rapid a rate to permit ready diffusion of the liberated hydrogen, loss of adhesion and blistering may occur. The general conclusion drawn from extensive testing on all types of aluminum, under a wide variety of conditions, is that paint adheres best to aluminum or aluminum alloy surfaces which are most nearly passive or corrosion resistant. Paint, therefore, under certain conditions, such as intermittent service in water, adheres better to pure aluminum than to some of the heat-treated alloys such as 17S. This conclusion would be of little practical use (since naturally the type of metal used is dictated mainly by the service conditions rather than its ability to take paint) were it not for the fact that the corrosion resistance of the surface can be modified and greatly improved by a variety of special surface treatments before painting.

The painting of aluminum and its alloys presents much the same problems as are involved in the painting of other metals. Surface preparation is an important factor, however, where protection against water and severely corrosive conditions is demanded. This is not a problem of roughening the surface, but of rendering it passive. Anodic coatings of certain types are effective in this respect, and good results are also secured with certain types of chemical cleaners. Chromate-containing paints make effective primers, and aluminum paints are also good. The best top-coat protection is rendered by aluminum paint.

The most effective of these treatments involves producing a thick and protective coating of oxide before painting. Sheet aluminum, as supplied to the trade, presents a smooth flat surface. The product known as flat sheet has a bright mirror-like surface as a result of finish-rolling between burnished steel rolls. Another type of sheet, known as gray plate, which has the reputation of taking and holding paint somewhat better than flat sheet, is finished by rolling against coated steel rolls. The steel rolls acquire a coating from contact with the aluminum itself; if this coating is allowed to remain on the rolls instead of being continuously removed, as with burnished rolls, the result is to give the gray-plate sheet a gray color and a microscopically rough surface. Because of the method of production, gray plate sells at a slightly lower price than flat sheet, and for purposes of painting is just as good and perhaps slightly better.

Surface Preparation

Aluminum to be painted should be free from oil, grease, dirt, and other foreign material, just as in the case of other metals; where greasy substances are to be removed, solvent cleaning can be employed. It is difficult on a commercial scale, however, to secure an oil-free surface in this manner because grease removed by the solvent remains in diluted form in the solvent used, and a thin film is left by evaporation. It is a more common practice, therefore, to remove thin films of oil by chemical treatment, such as with solutions of sodium phosphate and silicate. A variety of cleaners of this character have been developed which effectively clean aluminum without attacking it. In using them, it is important that all traces of the cleaner be removed by washing and that the piece be allowed to dry thoroughly before painting.

A still more effective surface preparation can be obtained by treatment with solutions containing phosphoric acid and alcohol. One such proprietary compound has had wide and successful use. It seems probable from experiments here that such a solution, in addition to cleaning the surface, leaves it in a passive condition as a result of the formation of insoluble aluminum phosphate. While such a surface treatment is not as effective as some of the oxide coating treatments to be described, nevertheless it is quite satisfactory and its lower cost dictates its use in many cases.

By a substantial margin the best surface preparation is obtained by oxide coating under conditions which give a hard, adherent, and impermeable oxide film on aluminum. The best films are obtained by anodic coating, and two general methods have been found satisfactory. The one method, known as the Bengough process (*2*), involves anodic coating in a 3 per cent solution of chromic acid under specified conditions of voltage and temperature. This method has found extensive application in the aircraft industry, where thin sections of duralumin have been given special protection thereby, either when used bare or followed by painting. The other method, known as the Alumilite process (*3*), has reached the stage of development where its use for this purpose can be recommended. This method involves anodic coating in electrolytes containing sulfuric acid, followed by special treatments which increase the protection rendered by the film. Oxide coatings, produced chemically without the aid of electric current, in general are not as impermeable or as protective as the anodic oxide coatings. However, coatings of this character which give satisfactory results are now under development and test.

The type of surface treatment which should be employed in any case is therefore determined not only by the metal to which it is to be applied and the character of the structure which is to be painted, but by the service conditions to which it is later to be exposed. In the painting of metal surfaces it seems to be almost axiomatic that some surface roughening is necessary or desirable if adequate paint adherence is to be secured. General experience here is that this factor has been much overrated, as adequate paint adherence for many purposes can be secured on smooth, bright, flat sheet if the paint selected is of the proper type. The degree of roughness of the surface is not the only controlling factor in paint adhesion in cases where moisture penetrates the film, as has just been explained. However, roughening the surface, as by sand-blasting, for example, undoubtedly provides better mechanical anchorage for a paint film, but once moisture has penetrated, corrosion may be more severe than if the original protective oxide film had not been removed by the sand-blasting process. If roughening of the surface is found necessary, it can advantageously be followed by anodic coating before painting. Sand-blasting is usually practical only for castings or very thick sections, since sheet may be warped in the process.

Accelerated Tests of Paints on Aluminum

An accelerated test has been developed for evaluating the various kinds of surface preparations, as well as the various types of paint which may be used, especially on the metal parts of seaplanes. Test specimens are built in the form of small boxes (10 × 10 × 7 inches), open at the bottom and vented at the top. These boxes are assembled by riveting and in a manner closely simulating actual aircraft practice. The surfaces of these boxes are prepared in various ways and paint coatings applied. In studying various methods of surface preparation, the same paint coating is used on all boxes. After the coating is thoroughly dry, the specimens are placed in large wooden tanks located on the roof of a plant at Edgewater, N. J., opposite New York, N. Y. Brackish water from the Hudson River is pumped into a supply tank which automatically drains, when full, to the first test tank, thence to the second and third tanks, and is finally discharged. The water in each tank rises to a level about 3 inches above the specimens before it passes to the next tank. The specimens are thus alternately wet and dried at about 45-minute intervals. The extreme lower portions of the specimens are continuously immersed. As the apparatus is located out of doors, the specimens are also continuously exposed to the weather in addition to alternate immersion in the salt water. This test, of course, cannot be made during freezing weather. In many instances failure of the poorer coatings occurs in 2 months, but many of the better coatings have withstood 2 or 3 years of such test. In Table I are summarized the results obtained with various types of surface preparation.

Table I. Effect of Surface Preparation for Painting 17ST Boxes[a]

(Two coats of aluminum paint applied to each specimen after preparing surface for paint)

Surface Preparation	Condition of Coating	Rating %
Anodic coating (Bengough process)	Excellent adherence of paint; practically no corrosion	100
Anodic coating (Alumilite process)	Excellent adherence of paint; practically no corrosion	100
Chemically applied oxide coating A	A few tiny paint blisters inside top face; good condition	90
Chemically applied oxide coating B	Slight blistering near water line and some above; very slight corrosion	80
Sand-blasted	Paint adherence fairly good; moderate corrosion	70
Cleaned with phosphoric acid–alcohol solution	Considerable fine paint blisters outside, larger inside; moderate corrosion	60
Caustic dip (etched with hot 5% NaOH soln., followed by immersion in cold 50–50 HNO_3)	Some peeling of paint; badly pitted and corroded inside, moderately outside	50
Solvent-cleaned (benzene)	Many large blisters, paint practically peeled off top face; considerable corrosion	40

[a] After accelerated test for 6 months.

In another series of tests of clear coatings on 17ST panels having various surface preparations, somewhat similar results were secured. These panels were given a single coat of a clear lacquer and exposed to the weather for 6 months, at a 45° angle facing south. The best surface preparation, as determined by metal protection and the appearance of the coating, was obtained with anodic coating. The other surface preparations were rated in the following order: cleaning with phosphoric acid–alcohol solution, buffing followed by solvent, solvent-cleaning, caustic dip, scratch-brushing. In this particular test there did not appear to be any marked difference between the solvent-cleaned and the etched surface after exposure for 6 months. Better adherence was also secured on the buffed surface than on the scratch-brushed surface.

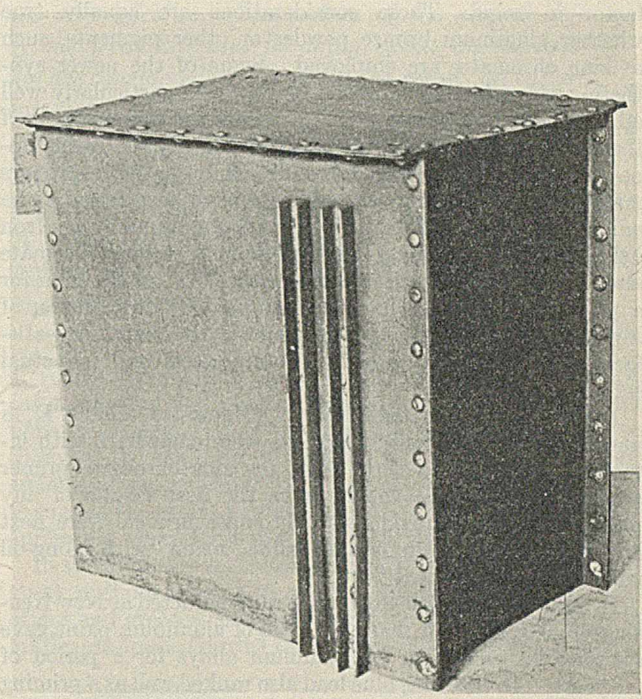


Figure 1. Anodically Coated 17ST Box with Two Coats of Aluminum Paint after Two Seasons (12 Months) in Edgewater Tests

(There was little change during the third season.)

Priming Paints for Aluminum

As previously indicated, it has not been found that special painting practice is required for painting aluminum under ordinary conditions of service. However, as in the case of steel or any other metal, the value of the painting system is dependent upon the primer employed. This is particularly true where severe exposure conditions are encountered. A good priming coat for aluminum, whether it be the commercially pure metal or one of the heat-treated alloys, should meet the following requirements: The primer should have good resistance to moisture penetration and hence prevent surface reaction. In some cases the primer should contain a pigment possessing corrosion-inhibitive qualities. It should also show satisfactory adhesion to the metal surface and at the same time present a surface permitting satisfactory adhesion of the succeeding coats of paint.

Meeting the requirement of a moisture-resistant film, aluminum paint made with a suitable vehicle stands high on the list of primers for aluminum. Aluminum paint also shows good adhesion to the metal and presents sufficient "tooth" for succeeding coats. For general application, aluminum paint has been found to give satisfactory service both as primer and top coat on aluminum.

From the standpoint of corrosion-inhibitive properties, the chromate pigments are, in general, most suitable (*1*, *4*, *5*). Of these, zinc chromate is probably the best. Excellent results have been obtained with zinc chromate primers on aluminum under particularly severe conditions of exposure.

The selection of the vehicle for a priming paint for aluminum is important. In the case of aluminum paint it has been found that a very long-oil varnish vehicle is most suitable. A more distensible paint film is desirable in painting aluminum than in the case of steel because of the slightly higher coefficient of expansion of aluminum. This high expansivity becomes a factor only after aging has markedly hardened and embrittled the paint film. The vehicle also is an important factor in determining the moisture-proofing properties of the paint and should be selected with this factor in mind. These considerations are equally true whether aluminum bronze powder or other pigments, such as zinc chromate, are employed. Some of the newer synthetic-resin vehicles have been found to be particularly well adapted as vehicles for priming paints for aluminum. Of these, varnishes made from Bakelite and glyptal resins appear to be the best so far tested. Zinc chromate primers made on a glyptal resin varnish base have been found to be among the most satisfactory primers for aluminum. Iron oxide primers containing certain amounts of zinc chromate also constitute an effective combination. A specification for a primer of this type has been adopted by the Bureau of Aeronautics of the Navy Department. It has given satisfactory performance both in exposure tests and in actual service.

In the box tests conducted at Edgewater (Table I), a number of different priming paints were compared, with interesting results. In these tests the zinc chromate primer made with a glyptal vehicle gave the best results of any primer tried. Iron oxide–zinc chromate primers were next in effectiveness. Aluminum paint made with long-oil varnish vehicles ranked third.

In a series of weather-exposure tests conducted at New Kensington, it was found that two coats of aluminum paint gave satisfactory protection to aluminum alloys for a period of 5.5 years. In this test, blue lead also ranked well as a priming paint. Red lead, however, was somewhat inferior to either of the other two paints mentioned. These tests were not extensive enough, however, to warrant rating the lead pigments for priming aluminum.

Finishing Coats for Aluminum

Once the metal is properly primed, any durable exterior paint or enamel may be employed for finishing coats. Here again, material long in oil is especially recommended; any desired color can be applied. Where the color of natural aluminum is satisfactory, aluminum paint will be found to give about the most satisfactory life of any coating. Whether used as a primer or top coat, aluminum paint will show its high moisture-proofing efficiency and opacity to light because of the specific nature of this film. The opaque metallic flakes of aluminum effectively retard the passage of light and moisture. The synthetic-resin enamels in various colors also form effective top coats. Lacquer enamels may also be used for this purpose, especially lacquer pigmented with aluminum powder. If lacquers are to be used, however, they should be of the most elastic type if satisfactory results are to be secured. The bituminous-base paints are frequently used on aluminum. Some of these paints with sufficient distensibility show satisfactory adherence as primers as well as top coats. They are high in moisture-proofing efficiency and are frequently used on the interior of duralumin seaplane floats and for waterproofing joints. They may be used alone where the black color is not objectionable, or may be pigmented with aluminum powder. Their tendency to alligator or check is greatly minimized when they are so treated. Because of their resistance to alkaline attack, they may be used in back-painting aluminum used in construction where it is in contact with mortar or other alkaline materials.

Generally speaking, a paint coating will show greater durability on aluminum than a similar paint coating applied to steel. A paint coating which may allow rust to become apparent on steel within 2 years may show good results on aluminum for twice that period before failure is noted. In some of the tests conducted at Edgewater, the built-up box-like test structures contained both aluminum alloy and steel, and the same paint was applied to all surfaces. The durability of the paint coating was appreciably greater on the aluminum alloy than on the steel surface. In the case of one box which had been given a chemically applied oxide coating prior to painting and then two coats of aluminum paint, the aluminum surface showed only a few slight blisters with tiny corrosion pits, whereas the steel was badly rusted. Even in the case of a box which had been merely cleaned with solvent, the aluminum was showing only small corrosion pits with some peeling of the paint film, whereas the steel again was badly rusted and the paint was peeling off in most places.

After three seasons of 6 months each of accelerated testing at Edgewater, two coats of aluminum paint over anodically coated 17ST were in excellent condition, showing but slight blistering at one end of the box with very slight pin-point corrosion pits on the top (Figure 1). Another anodically coated 17ST box, primed with zinc chromate followed by one coat of aluminum paint, was in even better condition, as it showed only slight corrosion in the joints of the box. These same coatings were applied to Alclad 17ST anodically treated and even better results were secured during the same length of exposure.

Clear Finishes on Aluminum

When it is necessary to maintain a polished finish on aluminum sheet or castings, transparent coatings may be employed. These coatings may be of either the lacquer or varnish type, but must be distensible and resistant to sunlight. Pyroxylin lacquers ordinarily lack in durability unless they contain appreciable quantities of light-resisting resins. Lacquers of this type are now available, however, and excellent results have been obtained in two-coat work for periods up to one year on panels exposed at 45° facing south.

The tendency of the ordinary type of varnish to turn yellow makes its use questionable for this purpose. However, some of the newer synthetic-resin varnishes have been found to resist yellowing satisfactorily for substantial periods. These varnishes are usually of the modified glycerol-phthalate type; they show even greater durability than the lacquers, and their adhesion to the aluminum surface is excellent. Certain of the vinyl resins have also given satisfactory performance.

Literature Cited

(1) Anonymous, *Proc. Am. Soc. Testing Materials*, 10, 73 (1910).

(2) Bengough, G. D., and Stuart, J. M., U. S. Patent 1,771,910 (July 29, 1930).

(3) Bengston, H., U. S. Patents 1,869,041–2; Gower, C. H. R., U. S. Patent 1,869,058 (July 26, 1932), and pending patents, all assigned to Aluminum Colors, Inc., Indianapolis, Ind.

(4) Gardner, H. A., *Am. Paint Varnish Mfrs.' Assoc., Sci. Sect. Circ.* 296 (1927).

(5) McCloud, J. L., Ind. Eng. Chem., 23, 1334 (1931).

Received August 29, 1932.

Preparation of Zinc and Zinc-Alloy Surfaces for Coating

H. A. Nelson and W. W. Kittelberger, New Jersey Zinc Company, Palmerton, Pa.

The discussion covers various types of zinc-coated steel, zinc sheet, zinc-alloy sheet, zinc-alloy die castings, etc. The service requirements considered range from structural surfaces to hardware and furnishings, the former being subject mainly to continuous exterior exposure, whereas the latter are limited to interior exposure and resistance to handling or only intermittent exterior exposure.

The conditions under which surface treatments may be desirable or necessary are discussed. Treatments that have been used include: cleansing with solvent washes, mechanical etching, chemical etching, formation of adherent deposits, and weathering. Each of these may be applied in numerous ways. Tests have shown that some of the proposed schemes are not at all effective, that others are very effective. The nature of the surface left by the treatment and its aging effects on the coating are considered as factors in the results on different metal bases.

Special primers may have merit and eliminate or largely reduce the necessity for drastic surface treatments. Consideration of good practice in primer formulation is just as essential for obtaining good adherence of finishes on zinc surfaces as on other metals.

THE painting of zinc and zinc-alloy surfaces is resorted to chiefly from decorative considerations. The element of protection enters where, occasionally, a second line of defense against corrosion is wanted as, for example, on galvanized iron.

New zinc surfaces are considered uncertain quantities from the standpoint of paint adherence, and the literature on paint abounds with suggestions for cleaning or pretreating to insure uniform results. However, few experimental results have been published, and these are based on the painting of structural galvanized iron and, to a limited extent, of sheet zinc. Although the coating of these materials, and especially galvanized iron, still is and will remain of importance, the development of new types of zinc-coated and zinc-alloy products has progressed so rapidly, and the recent developments in vehicle formulation have been so revolutionary, that the paint industry and painters now have many new combinations to consider. It is therefore the purpose of this paper to review the available information and, in so far as a limited amount of experimental work permits, in a preliminary way to suggest the extent to which the existing information may be applicable where these new materials are involved.

In the literature on the adherence of paint on zinc surfaces, many authors emphasize dangers arising from the presence of oils and greases, either adventitious due to handling, or as lubricants applied during the process of manufacture. Others blame the inherent smoothness of a fresh zinc surface. Still others emphasize characteristic physical properties, such as a relatively high coefficient of expansion, particularly in the case of sheet zinc which demands a higher degree of distensi-

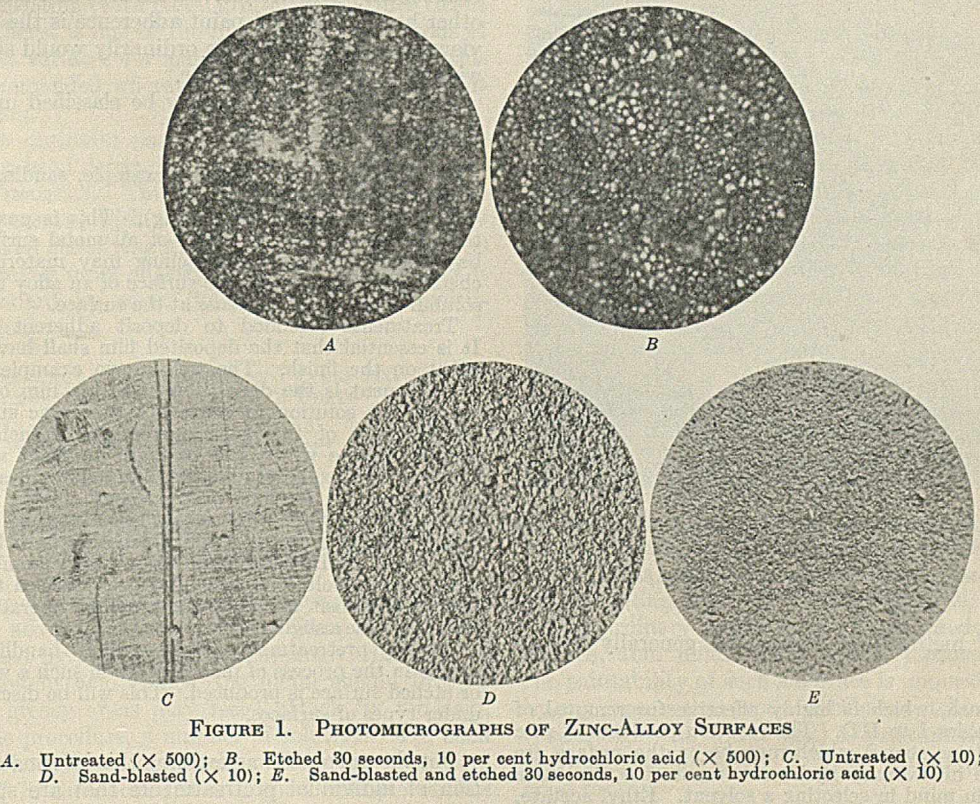


Figure 1. Photomicrographs of Zinc-Alloy Surfaces

A. Untreated (× 500); *B.* Etched 30 seconds, 10 per cent hydrochloric acid (× 500); *C.* Untreated (× 10); *D.* Sand-blasted (× 10); *E.* Sand-blasted and etched 30 seconds, 10 per cent hydrochloric acid (× 10)

TABLE I. IMPACT RESISTANCE MEASUREMENTS ON PANELS EXPOSED ON PALMERTON TEST FENCE[a] FOR 3.25 YEARS

(In revolutions of the impact hammer shaft, *3*)

METAL	CLEANED (IC), UNTREATED; GIVEN 2 COATS OF PAINT:		TREATMENT 10a; GIVEN 2 COATS OF PAINT:		TREATMENT 7; GIVEN 2 COATS OF PAINT:		TREATMENT 11; GIVEN 2 COATS OF PAINT:		TREATMENT 12; GIVEN 2 COATS OF PAINT:	
	A	B	A	B	A	B	A	B	A	B
Galvanized iron	(1)[b]	(2)	1721	1099	892	(1)	[c]	(3)	2198	103
Sheet zinc	(3)	(3)	(1)	189	(3)	(3)	[d]	(3)	127	...
Zilloy (shiny side)	(2)	(1)	2385	498	1136	(3)	169	(3)	1950	(3)
Zilloy (matte side)	(2)	(1)	1206	297	436	(2)	(3)	(3)	1106	224

[a] 45° south exposure.

[b] Since this test method does not permit numerical evaluations lower than 65, panels having values from 65 to 71 were regraded by other methods and rated thus: (1) best, (2) intermediate, (3) poorest. Do not compare the values for paint A with those for paint B, since the object has been to compare the surfaces and treating methods.

[c] Very bad flaking.

[d] Considerable flaking.

bility of the priming paint film than is normally allowed. Finally, progressive reactions between constituents of the vehicle and the zinc surface have been suggested.

It is probable that each of the above has, at one time or another, been responsible for individual failures, and it is just as likely that some combination of (1) the presence of a film of grease on (2) an excessively smooth surface, plus (3) lack of distensibility of the primer or (4) a reaction between priming vehicle and the zinc, has entered into most cases of poor adherence. Unfortunately, comparatively few such cases have been critically analyzed.

CLEANING

Thorough cleaning of any metal surface before applying an organic coating is universally accepted as a necessity for best results. This is true no matter how well prepared the surface may be in other respects.

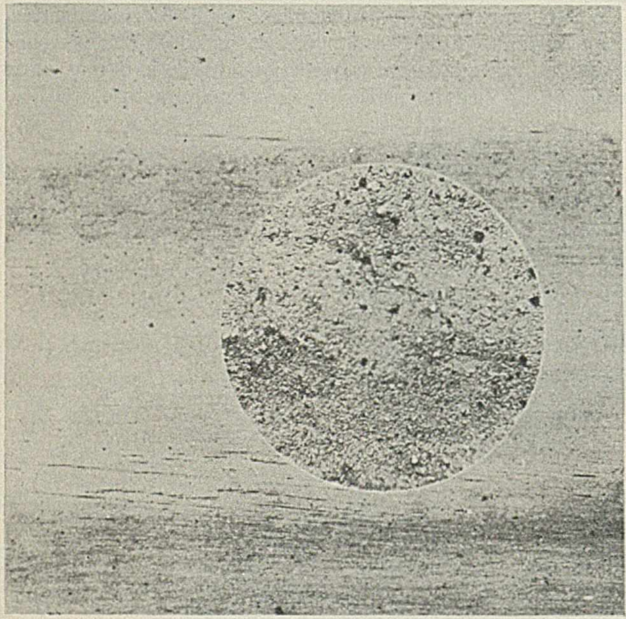


FIGURE 2. GALVANIZED-IRON STRUCTURE, PREWEATHERED AND FINISHED WITH TWO COATS OF GOOD ADHERING PAINT

(Paint A (Tables I, II, and IV) after 7.5 years of exposure to industrial conditions.)

Some cleaning methods in vogue and generally recommended are:

IC. Solvent wash, which is highly effective for removal of grease and oil (Tables I to III). The reaction products of zinc and acid greases (zinc soaps) which may be on the surface are not highly soluble in ordinary hydrocarbon solvents, and it is well to keep this in mind in selecting a solvent. Ethyl acetate, carbon tetrachloride, xylene, and solvents of their types are efficient for dissolving oil and grease as well as metal soaps.

IIC. Solution consisting of 250 cc. concentrated sodium carbonate solution and 500 cc. 3 per cent sodium silicate solution (Table III).

IIIC. Immersion for one minute at 70–80° C. in a solution consisting of 30 grams trisodium phosphate, 4 grams sodium hydroxide, and 2000 cc. water.

IVC. Electrolytic or cathodic cleaning. This method is extensively used in preparation for electroplating; its efficacy recommends it for use in the finishing industry. A widely used solution is 6 ounces of trisodium phosphate per gallon of water, maintained almost boiling hot while the article is made the cathode with a voltage that will cause violent gassing. One-half to two minutes, depending on the amount of grease and oil present, is sufficient for thorough cleansing.

The last three methods have the advantage that they tend to produce a slight etching of the surface, which is favorable to better adherence of any coating.

PRETREATING

The term "pretreatment" has come to mean some process of preparation other than mere removal of foreign material from the surface. Methods that clean and pretreat at the same time are also used.

In the case of iron and steel, pretreatment may, and usually is, intended to serve a dual purpose: Corrosion protection is the major aim, whereas increasing paint adherence is generally of secondary importance. With zinc and zinc alloys, on the other hand, increased paint adherence is the major object in view because these metals ordinarily would survive for years with no protection whatever.

Pretreatment schemes may be classified under one of the following general types:

Mechanical roughening—for example, sanding, sand-blasting, wire-brushing, etc.

Chemical roughening (etching). This is possible because of the microscopic heterogeneity of all metal surfaces. It should be remembered that acid-etching may materially change the chemical composition of the surface of an alloy through selective solubility of the constituents at the surface.

Treatments intended to deposit adherent inorganic films. It is essential that the deposited film shall have no deleterious effect on the finish. The well-known example of this type of pretreatment is the deposition of a thin film of copper from a copper salt solution in contact with a zinc surface. Another pretreatment of this type makes use of such compounds as sodium silicate which can be made to react with the zinc to produce an insoluble adherent film (zinc silicate in this case) on the metal. A third pretreatment of this type consists of treating the surface with certain organic acids, such as tartaric, oxalic, etc., in order to produce adherent films by reaction with the metal. A British patent (*2*) covers a number of such pretreatments. Solutions have also been devised to clean the surface and deposit inorganic films in one operation, effecting at the same time a slight etch.

Factory pretreatment. This involves handling the sheet or article in the process of manufacture in such a way that a rough or etched surface is produced. This will be discussed more fully under types of surfaces.

For the purpose of assembling this information, a classification of individual pretreatments that are suggested in the literature is given:

CHEMICAL SURFACE ROUGHENING OR ETCHING METHODS

1. Hydrochloric acid etch: 30 seconds in a 10 per cent solution (Table VI).

2. Phosphoric acid etch: 30 seconds in a 3 per cent solution (Tables V and VI).

3. Solution of: 1000 cc. water, 200 cc. commercial hydrochloric acid, and 20 grams ammonium nitrate (Table II).

3a. Mineral acid plus phosphoric acid (*1*).

PRETREATING DESIGNED BOTH TO CLEAN AND ETCH

4. Natural outdoor weathering for 3 to 12 months. While weathering is effective, it is also somewhat uncertain. For example, in some climates or under corrosive industrial atmospheric conditions, exposure for one month might suffice, whereas under milder conditions a much longer exposure is necessary. Also, all sides of a structure will not be equally weathered.

5. Sand-blasting (Tables III, V, and VI).

6. Wire-brushing, sanding, etc.

7. Solution for brush application consisting of: 65 parts (by volume) denatured alcohol, 30 parts toluene, 5 parts carbon tetrachloride, and 5 parts hydrochloric acid (Tables I, III, and IV).

TREATMENTS WHICH DEPOSIT INSOLUBLE FILMS ON THE METAL

8. Copper acetate solution: 6 ounces per gallon of water (Table III).

9. Solutions of other copper salts: chloride, sulfate, etc., which are generally made up to approximately 6 ounces per gallon of water.

MISCELLANEOUS PRETREATING SOLUTIONS

10. Proprietary solutions containing antimony, such as those sold under the trade names (a) Gun Metal Liquid, (b) Stibloy, (c) Solfo, etc. (Tables I and II).

11. Solution consisting of: 6.5 per cent sodium sulfate, 6.5 per cent ammonium nitrate, 1.5 per cent cadmium chloride, 7.5 per cent nitric acid, and 78.0 per cent water (Table I).

12. Solution consisting of: $^1/_8$ pound copper nitrate crystals, $^1/_8$ pound copper chloride crystals, $^1/_8$ pound ammonium chloride crystals, $^1/_8$ pint commercial concentrated hydrochloric acid, and 1 gallon water (Table I).

Experience has repeatedly indicated that the effectiveness of any pretreatment is, to a large extent, determined by the amount of roughening or by the increase in surface area which it produces. It must be remembered, however, that such a generalization holds only when the surfaces are perfectly clean. Hence blasting (with metal grit or sand), which cleans as well as roughens, is one of the most effective methods of preparing metal surfaces for painting (Table V), and this method is recommended wherever it is feasible to carry out such an operation.

Although the optimum particle size of grit or sand for blasting has not been determined, results favor the use of a relatively fine material. This is logical, since the amount of new surface created with a fine grit should be relatively greater. Material classifying at 80 to 100 mesh (through 80 on 100) has proved most effective on alloy castings and is considered standard by some finishers who have investigated the subject.

TABLE II. ADHERENCE EVALUATIONS[a] ON PANELS EXPOSED ON PALMERTON TEST FENCE FOR 2 YEARS

METAL	CLEANED (IC) UNTREATED; GIVEN 2 COATS OF PAINT: A	B	C	TREATMENT 3; GIVEN 2 COATS OF PAINT: A	B	C	TREATMENT 10b; GIVEN 2 COATS OF PAINT: A	B	C
Galvanized iron	3[b]	5	4	2.5	5	3.5	2.5	4.5	3.5
Sheet zinc	3	5	4	2.5	5	3.5	2.5	4.5	3

[a] Graded by scraping the films away from the metal with a knife.

[b] Adherence: 1, very good; 2, good; 3, fair; 4, poor; and 5, very poor.

Chemical etches are probably next in order of effectiveness and have the advantage that most of them can be conveniently applied by brushing on, or dipping. However, in the case of straight acid etches, the metal should first be cleaned, since greasy areas may resist attack by the acid. To simplify the procedure, a number of solutions have been devised which both clean and etch in the same operation. Pretreatment 7 in the above list is a good example of this type of pretreating solution. Furthermore, after using an etching solution of any kind, it is essential to remove water-soluble salts from the metal surfaces, either by washing with water or by a brisk brushing after the surface has dried.

TABLE III. GRADING OF PANELS VISUALLY ON BASIS OF FLAKING OF PAINT FROM METAL AFTER EXPOSURE ON TEST FENCE 2.25 YEARS

CLEANING OR PRETREATMENT	METAL	PRIMING COAT A + 2 COATS PAINT: 1[a]	2	PRIMING COAT B + 2 COATS PAINT: 1	2	PRIMING COAT C + 2 COATS PAINT: 1	2
IC (benzene)	Galvanized iron	1[b]	1	2	2	4	5
	Sheet zinc	..	..	..	..	5	5
8	Galvanized iron	3	2	3	4	2	4
	Sheet zinc	..	..	..	..	5	5
IC & 8	Galvanized iron	3	1	2	3	..	..
	Sheet zinc	..	..	..	..	..	..
12	Galvanized iron	3	3	2	5	..	..
	Sheet zinc	..	..	..	..	..	..
7	Galvanized iron	2	2	1	2	..	..
	Sheet zinc	..	..	..	..	..	..
IIC	Galvanized iron	1	3	1	4	1	5
	Sheet zinc	..	..	..	..	5	5
4	Galvanized iron	1	1	1	3	2	5
	Sheet zinc	..	..	..	..	4	5
5	Galvanized iron	1	1	1	2	1	3
	Sheet zinc	..	..	..	..	1	4

[a] Paints 1 and 2 are representative white exterior house paints which were used over the primers A, B, and C.

[b] Flaking: 1, none whatever; 2, slight; 3, considerable; 4, bad; and 5, very bad.

Care is necessary in the use of acid etches on zinc alloys containing copper (Milloy (all types), Zilloy, Zamak), since the treatment may leave a layer of the undissolved copper on the surface in a powdery form. In any case, it is well to avoid the use of pretreatments designed to deposit films of copper on the metal. Such films are erratic in their nature and seem to have a general tendency to be loosely adherent and powdery. If such treatments are used, the removal of all powdery material must be assured by vigorous brushing or by scrubbing with water.

TABLE IV. INITIAL IMPACT RESISTANCE OF FINISHES ON FACTORY-PRETREATED GALVANIZED IRON

(In revolutions of impact hammer shaft, *3*)

METAL	ONE COAT AIR-DRY METAL-PROTECTIVE PAINT D	BAKED FINISHING SYSTEM PRIMER AND ONE COAT OF ENAMEL
Galvanized iron	606	4560
Pretreated (method 7) galvanized iron	618	184
Factory-pretreated galvanized iron No. 1	902	2133
Factory-pretreated galvanized iron No. 2	1233	13000

It has been argued in favor of certain chemical treatments which leave adherent deposits, that they possess one advantage—namely, better inherent adhesion of paint vehicles than on the zinc surface, or less reaction between the surface and the priming vehicle. Direct experimental evidence on this subject is lacking in this laboratory. The question of possible reactions between zinc surfaces (or surfaces formed by pretreatments) and priming-coat vehicles is one now under investigation, so that no further discussion of the subject will be attempted in this presentation.

TYPES OF ZINC SURFACES AND REQUIREMENTS FOR EFFECTIVE TREATING

The increasing number of types of zinc coatings and zinc articles that are encountered by the finisher has been mentioned. In the first group to be discussed are the different coated irons and steels, which differ in the manner in which the protecting layer of zinc has been applied.

The ordinary galvanizing process produces a continuous surface, and, unless some special priming system is used, the paintability of such a surface is unquestionably improved by any process that produces efficient etching. Sand-blasting (preferably with a fine grit) is recommended, but chemical treatments (especially 1, 2, 7, and 10) can be made to produce good results.

Sherardized surfaces, produced by tumbling heated articles in metallic zinc powder (zinc dust), are inherently rough and present no particular problem if a primer of reasonably good distensible properties is used.

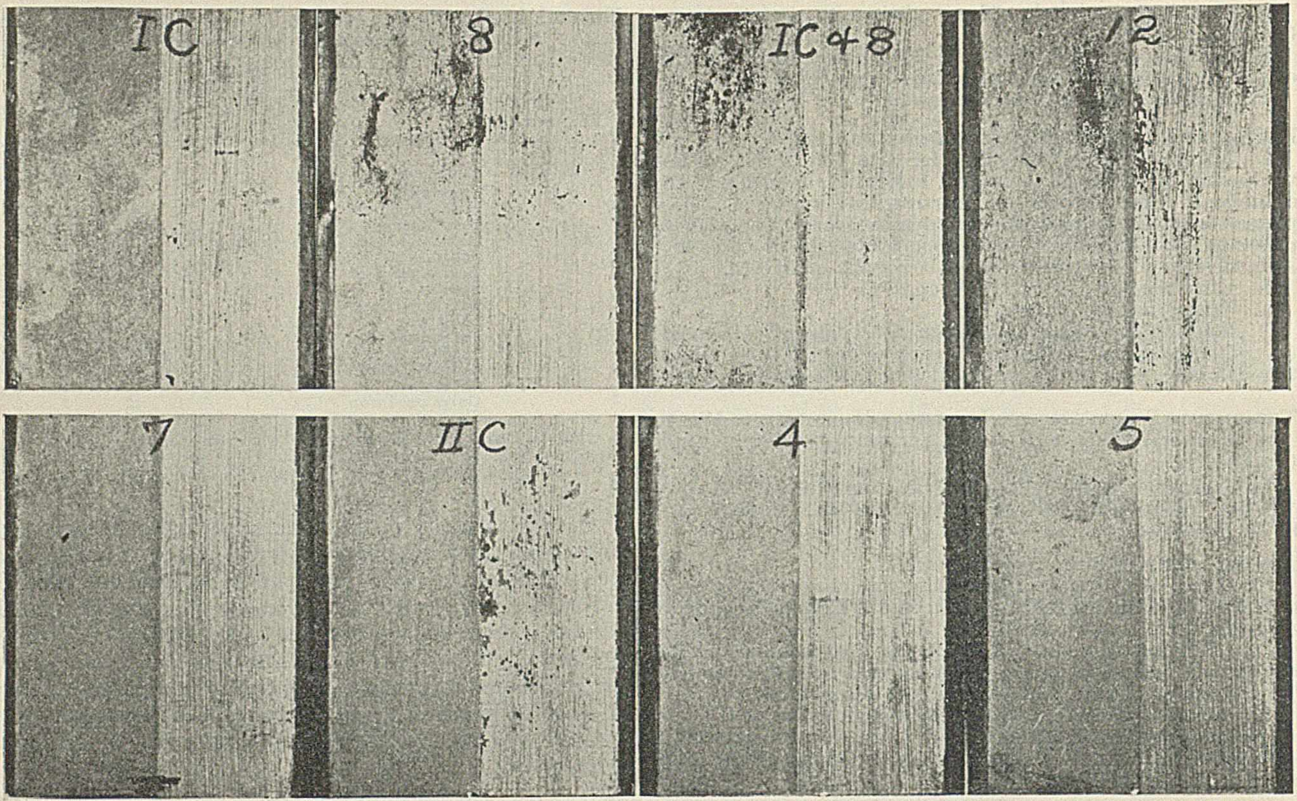


Figure 3. Panels Primed with Paint A (See Caption to Figure 4)

Electroplated (electrogalvanized) surfaces are generally quite rough and should be easily finished, but difficulty may be encountered because of occluded gases in the metal deposit, which may cause blistering and peeling troubles where baked finishes are applied; they have been known to do so even with air-dried finishes. Preheating the metal to a temperature well above the baking temperature used in the finishing process is usually effective in overcoming this difficulty, but it sometimes persists even then. The use of distensible low-temperature bake or air-drying primers is suggested.

Producers of galvanized iron have recognized the troubles of the painter with the normal product and have sought to meet the situation with factory-pretreated products (Table IV) which are generally covered by patents. One product is annealed in the process of manufacture to produce a rough matte surface. The painting characteristics of such surfaces have generally been found to be satisfactory without any further treatment, except to make sure that the surface is clean.

Table V. Initial Impact Resistance of Finishes on Sheet Zinc

(In revolutions of impact hammer shaft, *3*)

Treatment	One Coat Air-Dry Metal-Protective Paint D	Baked Finishing System Primer and One Coat of Enamel
Cleaned with ethyl acetate	538	2215
Cleaned with ethyl acetate, etched with H_3PO_4 (method 1)	3267	5562
Sand-blasted	5122	8182

Other surfaces of this type are produced by spraying the iron base with a mixture of metallic zinc powder and a volatile binder. This is subsequently heated sufficiently to produce an adherent metal coating. Such coatings are quite discontinuous and are usually not intended for exposure without painting. Experience with them is more limited, but a few laboratory tests have indicated satisfactory paint adherence with the better grades.

Ordinary sheet zinc presents a difficult problem in finishing. In addition to a high coefficient of expansion, it is subject to easy deformation, which taxes any nondistensible coating. Sand-blasting is recommended as being most effective, although chemical pretreatments have also produced reasonably good results (Table V).

The recent development of stiff alloys (Zilloy, etc.) has apparently provided sheet-zinc products which respond well to a number of pretreatments (Table I), besides showing better paint-holding qualities even in the untreated form.

Table VI. Initial[a] Impact Resistance Measurements on Zamak Die Castings Finished with Two Baked Coats of Black Japan

Surface Treatment	Revolutions of Impact Hammer Shaft
As cast, cleaned with ethyl acetate	1,321
As cast, cathodically cleaned (method IVC)	6,739
As cast, etched with H_3PO_4 (method 2)	9,878
As cast, etched with HCl (method 1)	13,240
Sand-blasted	27,944
Sand-blasted, etched with H_3PO_4 (method 2)	32,247
Sand-blasted, etched with HCl (method 1)	50,788

[a] Data on aged specimens not yet available.

Zinc die castings require rather unusual consideration because many die-cast articles when finished are subject to more or less severe conditions of handling, etc. Properly treated, however, they do show exceptionally high initial impact resistance, as indicated by the results in Table VI. Sand-blasting is the recommended pretreatment, but this can apparently be supplemented with a chemical treatment to good advantage.

To select a satisfactory pretreating system for a given job requires an analysis of the use for which the article is intended. With a good priming system, die castings should not, in general, require anything more than efficient cleaning with a slight etching. Sheet products, however, generally need some sort of pretreatment, unless service conditions are not severe, or a finishing material of high adhering qualities is used. Extremely severe service conditions would necessitate the best of pretreatments, such as sand-blasting, followed by a high-grade adherent finish.

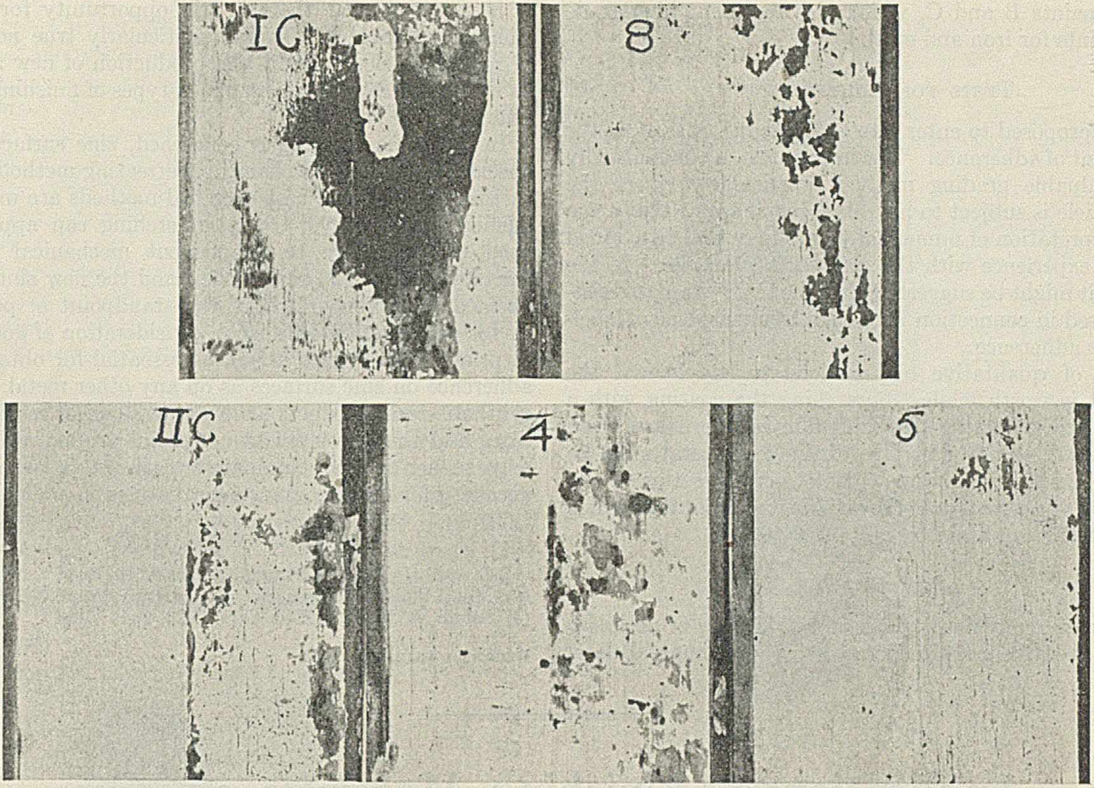


Figure 4. Panels Primed with Paint C

Figures 3 and 4 are representative galvanized-iron panels of test series after exposure 2.25 years at angle of 45° facing south.

Left halves finished with two coats of paint, right halves finished with two coats of paint 2 (Table III). (Panel numbers are keys to cleaning and pretreating systems mentioned in text).

Coating Materials and Their Application

Experience with finishing materials on zinc surfaces has, until quite recently, been based almost exclusively on the usual oil and natural-resin base primers of the air-drying and baking types. It is believed that this experience generally favors the long-oil type primers. This is particularly true for the painting of structural materials such as galvanized iron, where adherence tests favor oil-vehicle type paints as against the ordinary run of spar varnishes.

With the recent advent of synthetic-resin type vehicles, new and still relatively unknown factors demand consideration. However, the limited experience with primers of this type has shown interesting possibilities, so one can predict that the change from the older types to the new synthetic-resin primers and enamels will in many cases prove advantageous. An example may be cited where recently several commercial samples of synthetic-resin primers of relatively low-temperature baking were obtained offhand which produced better adherence on sand-blasted zinc die castings than had been obtained on brass with a higher baking finish of what had been considered good adhering qualities.

In baking finishes on zinc and zinc-alloy articles, it should be remembered that zinc is a metal of relatively low melting point, and, although the usual baking temperatures are well below the melting point of the metal, it is possible to injure seriously some of its physical properties. It is rather difficult to set any definite limits as to permissible baking temperatures and times, because these vary to a certain extent with the size and shape of the article. Furthermore, changes in one or more of the physical properties of the metal may be of no importance so far as a particular article is concerned.

However, a few guiding rules might be mentioned. In the case of the 4 per cent aluminum–3 per cent copper–0.05 per cent magnesium alloy (Zamak No. 2), 2 hours at 120° C. (248° F.) will ordinarily be a safe limit. For the more recently introduced 4 per cent aluminum–0.05 per cent magnesium alloy (Zamak No. 3), the safe limit is somewhat higher, but in some cases a limit as low as 150° C. (302° F.) is necessary. These temperatures are nominal oven temperatures and allow for the temperature fluctuations and inequalities that are likely to be encountered in commercial practice.

The limiting temperature for the bake-enameling of rolled zinc and zinc-alloy sheet will vary with the composition of the metal and the amount of cold-working present, and with the requirements for properties in the finished object. As a general rule, all of these materials will give good results in a 2-hour[1] treatment at 100–150° C. (212–302° F.) The most satisfactory and safest way of handling the situation is to consult the manufacturer of the metal who will be able to furnish data to fit the particular case.

Until comparatively recently it has been general practice to use much the same priming materials on practically all structural metals—iron, steel, galvanized iron, or zinc sheet—although their ordinary rust-inhibitive properties on iron and steel may be of little significance on zinc and zinc-alloy surfaces. Many of these priming paints, which are highly efficient on steel, make a relatively poor showing of adherence on zinc surfaces. A peculiar and as yet not fully explained phenomenon is the rather marked improvement in adherence often obtained where metallic zinc powder is used in primers for structural zinc surfaces subject to severe weathering. This is demonstrated by paint A (Tables I and II and Figure 2) in which the vehicle (largely raw linseed oil) is the same as

---

[1] This means a total time of 2 hours and may be made up of several shorter baking periods.

applied over zinc may thus be a continuation of such behavior. The fact that there is a definite chemical action taking place is evident both by the change effected in the zinc surface after being in contact with a paint film and the complete alteration in the characteristics of the film.

In the case of a pyroxylin material, there is apparently a decomposition of the nitrocellulose, and the free acid liberated reacts with the zinc surface. Zinc in this case probably acts as a catalyst.

Assuming that there is a chemical action taking place between a paint film and a zinc surface, the solution to the problem seems to be: (1) to incorporate an inhibitor into the paint or (2) to change the nature of the zinc surface.

USE OF INHIBITORS

Work with inhibitors in this laboratory has been mostly confined to the pyroxylin type of materials. The addition of a small amount of amyl borate to a lacquer has been found to retard greatly its decomposition when applied over zinc. This effect is shown by Figure 1. Half of this panel (*B*) is coated with a regular nitrocellulose lacquer, and the other half (*A*) is coated with the same material to which about 1 per cent of amyl borate has been added. It can be seen by bending the ends of this panel that the film containing the amyl borate has remained flexible with good adhesion, whereas the other film has become quite brittle. It is possible that by the use of such an inhibitor nitrocellulose lacquers may be prepared that will show entirely satisfactory adhesion over untreated zinc surfaces. However, to date it is practically accepted that zinc surfaces must be treated either mechanically or chemically before the application of finishing materials.

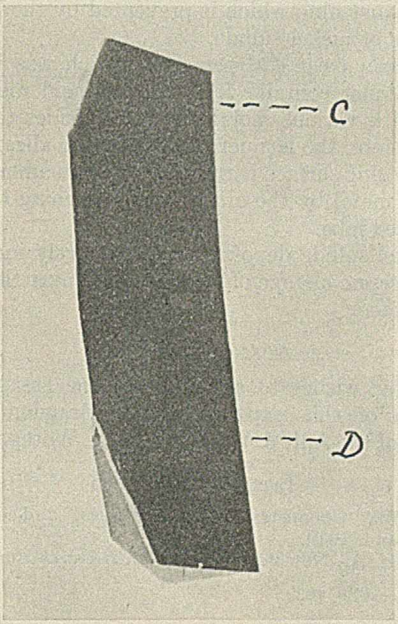


FIGURE 2. EFFECT OF CHEMICALLY PRIMING ZINC SURFACE

MECHANICAL TREATMENT

The mechanical method generally used is sand-blasting. This operation roughens the surface, forming pits to which a paint can anchor itself more firmly. The initial adhesion is considerably improved by this method. However, unless the paint is applied immediately after the operation, the decomposition is not retarded. This fact is illustrated by the following experiment: A pyroxylin lacquer was applied over a zinc strip, a section of which was scratch-brushed with a fine wire brush. The portion of the film over the scratched surface took considerably longer to break down than that portion over the untreated section. However, in repeating the experiment and allowing an interval of several days before applying the lacquer, little difference was noted in the time for the breakdown of the respective films.

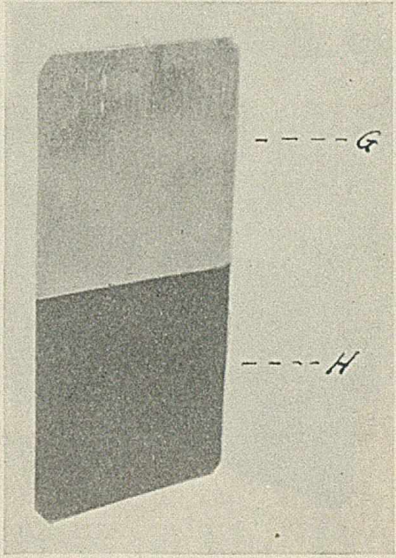


FIGURE 3. EFFECT OF ZINC ON ALIZARIN

CHEMICAL TREATMENTS

The same roughening of the surface is accomplished chemically by etching. Various solutions are used for this purpose, each claiming certain advantages and effects. Perhaps the most effective of these solutions is a dilute chromic acid bath containing a small amount of nitric acid. A practical formula is: 135 grams sodium dichromate, 400 cc. nitric acid, 600 cc. sulfuric acid, and 20 liters water. Contrary to most etching solutions, this gives an even crystalline ground which will not show under a paint. A brown scum usually appears on the surface when the metal comes from this solution. However, immersion for about a minute in a dilute nitric and sulfuric acid solution readily removes this scum. The plate is then washed free from acid and dried. This drying is important. The water must either be wiped off by means of sawdust or any other absorbing medium, or be displaced by dipping the plate into a lacquer thinner that is sufficiently miscible with water so as to allow the plate to dry free from contact with water. This process has the same disadvantage as sand-blasting in that it is often quite impractical to apply the finishing material immediately after treatment.

Another method of treating zinc surfaces is by the deposition of a metal or a metal compound on the surface. By this method the paint film is prevented from coming in direct contact with the zinc. The deposition is accomplished either by electroplating or by simple immersion. The immersion method which takes advantage of the potential difference set up in the solution is considerably less expensive and simpler, and for these reasons is most widely used. The most popular solution of this type is a dilute copper sulfate solution. It can be brushed over the zinc surface, or the object can be immersed in the solution. The copper in this case is replaced by the zinc (forming zinc sulfate) and the reduced copper deposits on the surface.

Salts of antimony, arsenic, and nickel are also used for this purpose and are marketed under various trade names. Their effectiveness, although satisfactory while it lasts, is not permanent. The metal deposited is eventually absorbed or gradually alloys with the other parts of the zinc, forming a uniform alloy having a high zinc ratio. Although in a less degree, this alloy effects a decomposition of the paint film in the same way as zinc itself. Brass, electrodeposited over zinc, has been known to disappear apparently over a period of several months.

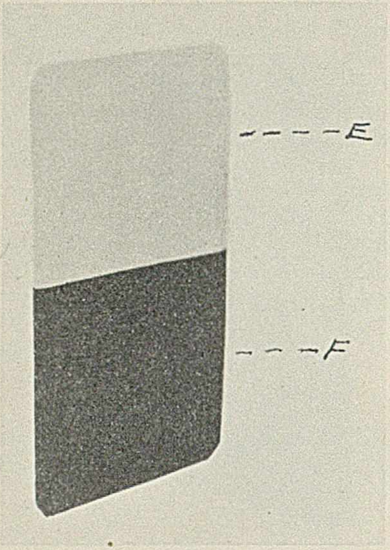


Figure 4. Panel Similar to Figure 3 except that Clear Lacquer Does Not Contain Alizarin

So far, the most effective method is the deposition of a metal compound which will not alloy with the zinc and at the same time will be inert to paint films. Nickel sulfide is a good example of such a deposit. This system also takes advantage of the difference of potential set up between the metal ion and the zinc. As described above, nickel will deposit on zinc from its salt by simple immersion, and in the presence of hydrogen sulfide will readily form nickel sulfide. Therefore, by incorporating, for example, sodium sulfocyanide in the solution, the free acid in the solution will react with it, forming hydrogen sulfide which will change the nature of the nickel deposit accordingly. It is essential that the metal be free from oil and grease before it receives this treatment. This can be done in various ways. A caustic soda solution, vapor bath, and cleaning with lacquer thinners all give satisfactory results as preliminary treatments to the chemical-priming solution.

The chemical-priming deposit has excellent adhesion and flexibility, provided it is not put on too thick. A satisfactory deposit can be obtained in about 30 seconds. However, the speed of deposition is proportional to the temperature and concentration of the bath.

The effectiveness of this method is shown by Figure 2. Half of this panel (*C*) was chemically primed with nickel sulfide and the other half (*D*) left untreated; a nitrocellulose lacquer was applied over this panel. By bending the ends, it can readily be seen that the portion of the film over the chemically primed surface has not changed, whereas the portion over the untreated surface has become quite brittle and has lost practically all its adhesive properties.

Figure 3, a section of which was also chemically primed, was coated with a clear pyroxylin lacquer to which was added a small amount of alizarin, giving it an amber tint. Over the untreated section (*G*) the film turned violet; over the chemically treated section (*H*) the original amber color was retained. This is an additional indication of reaction between the zinc and the lacquer film, which is prevented by the interposition of the layer of nickel sulfide.

The alizarin paste (20 per cent) which was incorporated into the lacquer contains free hydroxy acid radicals, which combine with various metals or metal oxides to form lakes (*1*). Therefore, the lacquer containing the alizarin when applied to the zinc surface permitted a certain amount of attack of the zinc metal by the alizarin acid, forming the purple or violet colored lake.

The nickel sulfide deposit, being relatively inert, does not react; hence, no change of color resulted over the chemically primed surface.

Acknowledgment

The writer wishes to acknowledge the assistance in the preparation of this paper of C. R. Bragdon and E. W. McMullen of the Ault & Wiborg Varnish Works.

Literature Cited

(1) Fay, I. W., "Chemistry of Coal Tar Dyes," 2nd ed., p. 349, Van Nostrand, 1919.
(2) Nelson, H. A., New Jersey Zinc Co., *Research Bull.*, 1930, 5.

Received August 29, 1932.

[End of Symposium]

Remedies Outlined for European Paper Industry

Various remedies being tried by the European paper industry to meet prevailing adverse conditions include cartels, educational and advertising campaigns, special organizations to regulate production and exports, and appeals urging the use of "home" products, according to the Department of Commerce.

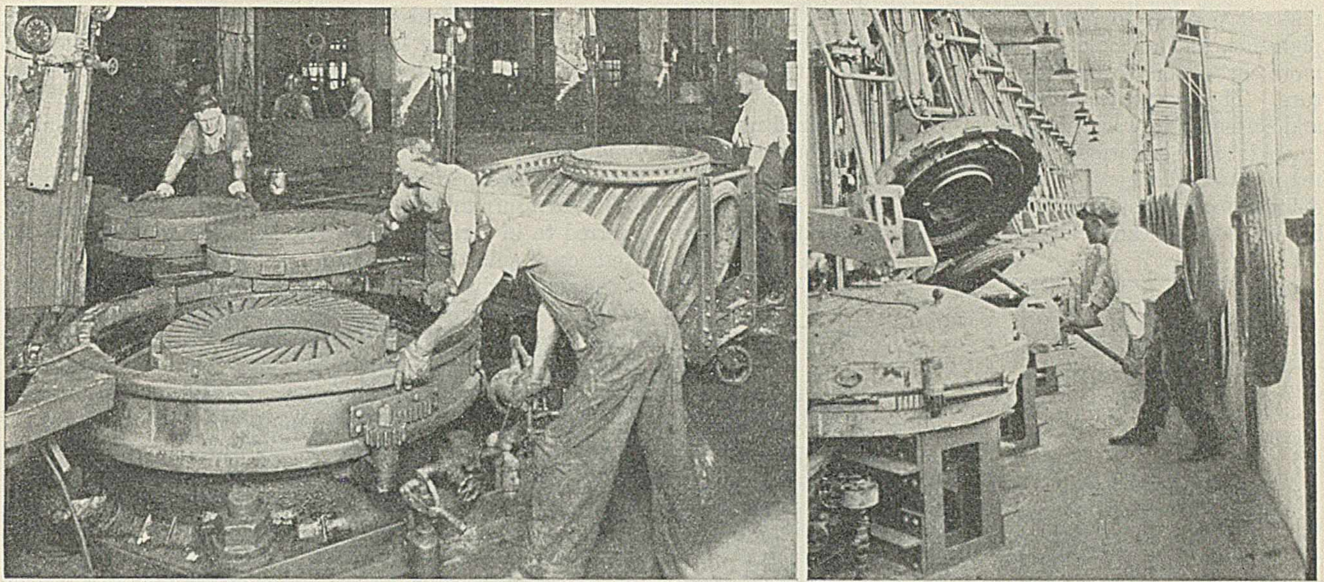
The German paper industry is seeking to improve its position by further cartelization and recent discussion among the leading manufacturers is said to have brought about a rise of 5 per cent in the price of writing and printing papers and 10 to 15 per cent in that of wrapping paper. Proposals have also been put forward in Germany to regulate production by a reduction in the number of working days and to require manufacturers to adhere to their particular lines.

An extensive educational and advertising campaign has been undertaken by the Czechoslovak paper and board cartels, designed to increase the domestic demand for paper and paper products, especially wrapping paper and containers for foodstuffs. Demonstrations of the sanitary handling of foodstuffs, especially milk and dairy products, are being carried on and special instructions are soon to be issued by the Ministry of Public Health prohibiting the sale of milk from open containers and requiring the use of glass or paper bottles. The instructions also require the wrapping of butter and cheese in grease-proof or parchment papers.

Kraft paper manufacturers of Norway, Sweden, and Finland have reached an agreement for regulating production and export. The total production involved is approximately 250,000 metric tons, of which 40,000 tons have been allotted to Norway, 180,000 tons to Sweden, and 30,000 tons to Finland. The new combination will operate under the name "Scankraft."

Swedish and Finnish kraft pulp manufacturers have also established a special organization to promote the use of fiber containers throughout Europe. The considerable increase in the production of sulfate pulp during recent years, particularly in Sweden and Finland, has made it necessary to find new uses for this product. It is thought that a wider market for fiber shipping containers would offer a solution.

An appeal to Spanish newspapers to purchase paper of domestic manufacture has been published in Madrid newspapers, stating that Spanish mills are being closed for lack of orders and national labor and industry merit the purchase of products manufactured in Spain. It is further pointed out that Spanish paper prices are no higher than those of the imported product and that the quality is better.



LEFT: OLD METHOD OF VULCANIZING TIRES IN STACKS IN VERTICAL AUTOCLAVES; RIGHT: NEW METHOD OF VULCANIZING TIRES IN INDIVIDUAL STEAM-JACKETED WATCHCASE MOLDS

A Century of Technical Progress in the Rubber Industry

NORMAN A. SHEPARD, Firestone Tire and Rubber Company, Akron, Ohio

The rubber industry really began with the discovery of vulcanization in 1839. Some rubber manufacturing was done prior to that date, but the products were so unstable that little progress was made. Vulcanization, reclaiming, the value of acid compounding ingredients, organic accelerators, antioxidants, and reënforcing pigments have all been developments of the last hundred years. These advances are discussed here, together with the important part which oxygen plays in the life history of rubber and rubber products.

ALTHOUGH the rubber business is considerably more than a century old, the first factory probably having been started during the first few years of the nineteenth century, the business could hardly be dignified with the name of "industry" until the discovery of vulcanization in 1839. The rubber industry may, therefore, be considered as not yet one hundred years old, and, in describing a century of technical progress in this field, all the important advances in the industry, including vulcanization itself, must logically be included. It is appropriate at this time to take a retrospective view of the advances in rubber technology. "A Century of Progress" is rapidly taking concrete form in Chicago, where the buildings of the 1933 World's Fair are nearing completion.

Technology is a broad term, and perhaps ill-advisedly chosen for the title of this article. If one should attempt to cover the subject from the standpoint of chemical, physical, and engineering technology, mere enumeration of the advances would result in a paper of ponderous length, as it would involve not only advances in the art of compounding rubber, but also the advances in the design and construction of the textiles used with rubber, the advances in design of equipment and machinery used in the fabrication of rubber articles, and the evolution of the design of the articles themselves. The discussion in this paper will therefore be confined to some of the major chemical, physical, and physico-chemical discoveries connected with rubber itself; a general idea of the engineering features of the manufacturing processes may be obtained from the accompanying photographs.

VULCANIZATION

It has been stated that the industry had its real beginning in the discovery of vulcanization. This process, involving the heating of rubber with sulfur, is too well known to require any elaborate description.

What it accomplished is perhaps not such common knowledge. The crude rubber of commerce, even in its present improved form as prepared on scientifically managed plantations, leaves much to be desired in physical properties. As a highly complex colloidal material with marked chemical unsaturation, and containing, in addition to the rubber hydrocarbon, up to 7 per cent of non-rubber constituents (protein, resins, acid materials, etc.), it is especially subject to both chemical and physical changes. It is attacked by the oxygen of the air, first being converted into a sticky product, and later becoming hard and brittle as the process of oxidation advances. Rubber is subject to marked changes with change in temperature, losing much of its elasticity when held at temperatures only slightly below the freezing point of water, and becoming soft and plastic at summer temperatures. One may question these statements in view of the quite satisfactory service obtained from crepe soling such as that used on sport shoes, but such soling has received no "working" or mastication on mills and is not blended with compounding ingredients of any sort. When subjected to plasticizing to used with paints B and C, which also represent high-grade priming paints for iron and steel.

Tests for Adherence

It is not proposed to enter into a detailed discussion of the measurement of adherence. The impact test (*3*) undoubtedly offers a valuable grading method, particularly where the finished article is subject to handling, but it seems that a too literal interpretation of numerical values may well be avoided until more experience with the method is available. In the meantime, it might be suggested that the term "impact resistance" be used in connection with such results instead of labeling them as adherence.

The use of qualitative observations to supplement the impact test is worth while. Scratching the coating with a knife and noting whether the paint film can be flaked clean from the metal, or if the surface of the base metal must be abraded in order to remove a complete cross section of the film, furnishes information to the experienced paint man which may be difficult to obtain by any other test.

Summary

From the above review, which at this time is of necessity based on a relatively limited amount of experimental data, it is apparent that there is still opportunity for investigation of the subject. This is particularly true now in view of recent developments in the production of new zinc alloys, as well as the much wider range of types of finishing materials obtainable.

In so far as cleaning is concerned, zinc surfaces offer no special problems. Mechanical pretreating methods are quite satisfactory and the best chemical methods are undoubtedly equally satisfactory. Chemical etching can apparently be used to advantage to supplement mechanical treatment. Factory-treated galvanized irons and the new zinc alloys are decided improvements from the standpoint of paintability. As for the selection of finishes, consideration of good practice in primer formulation is just as essential for obtaining good adherence on zinc surfaces as on any other metal. The new synthetic-resin products have shown superior results in many cases and the development of special primers will undoubtedly, sooner or later, eliminate or reduce to a large extent the necessity for the use of surface treatments.

Literature Cited

(1) Gravell, J. H., U. S. Patent 1,221,046 (1917).
(2) Metal Finishing Research Corp., British Patent 362,956 (1930).
(3) Schuh, A. E., Ind. Eng. Chem., 23, 1346 (1931).

Received August 29, 1932.

Application of Finishing Materials on Zinc

Milford H. Corbin, The Ault & Wiborg Varnish Works, Inc., Cincinnati, Ohio

Although zinc is one of the oldest metals, its use for structural and ornamental purposes has been slow in developing. One of the factors responsible for this retardation is probably related to the difficulties presented in the application of finishing materials to its surface.

Pyroxylin and oleoresinous types of finishing materials both exhibit certain signs of decomposition or breakdown in contact with metallic zinc, losing their flexibility and adhesion. This decomposition is proportional in extent to the time in contact. There have been many theories attempting to explain this behavior and various treatments offered to overcome the difficulties. Nevertheless, zinc still presents its age-old problems of finishing. Cadmium, which has come into use much more recently, is so closely related to zinc that its behavior is similar and similar remedies may be applied.

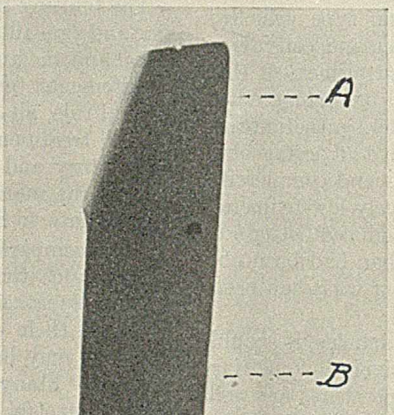


Figure 1. Effect of Inhibitors in Nitrocellulose Lacquer

Causes of Breakdown of Paint Films

One theory, attempting to explain the breakdown of paint films in contact with zinc, attributes the cause to occluded oxygen (or other gases) which, upon aging, comes to the surface and undermines the paint film, thus destroying its adhesion. In the case of oleoresinous materials, a possible additional cause of breakdown of the film is further oxidation, which would tend to increase the brittleness of the film. If this were the case, it would logically follow that paint would gradually lose its adhesion when applied to buffed metallic surfaces, since it has been proved that during the buffing operation a certain amount of oxygen is occluded by the surface. But this is not true. Paint films do not deteriorate more over buffed than they do over unbuffed surfaces.

Another theory (*2*) mentions that zinc presents a smooth surface which offers no pits or pores into which a paint can anchor itself. This probably explains why it is difficult to make paints initially adhere to zinc surfaces, but bears no connection with the apparent breakdown of the film.

The relatively high coefficient of expansion is also offered as a cause (*2*) for the lack of adhesion of paint films to zinc. Nevertheless, films possessing an unusually high degree of elasticity still become brittle and lose their adhesion when applied on zinc.

Most theories are similar to those mentioned above, attempting to explain the difficulties upon physical grounds, whereas the action of a paint film in contact with zinc indicates that a definite chemical reaction takes place.

Zinc is a highly electropositive metal and, like aluminum, readily forms an oxide when exposed to air and moisture. Since zinc oxide pigments, when incorporated into the usual type of oleoresinous vehicles, cause a hardening effect (decreasing the flexibility and distensibility of the film), there is some ground for the belief that the action of zinc or some compound of zinc causes a similar behavior (whether of accelerated polymerization or otherwise) comparable to that of a metal drier. The breakdown of an oil base material when make it possible to incorporate the vulcanizing agents and pigments, and to mold and shape it, rubber becomes much more susceptible to oxidation and to change with temperature. The proverbial stiffening and cracking in cold weather and softening in warm weather of the unvulcanized raincoat (mackintosh) of former days was largely attributed to the temperature changes. It is probable that oxidation played a definite part in the deterioration, as unoxidized rubber that has not been vulcanized can be frozen to temperatures as low as −50° C. with carbon dioxide snow, and held at the low temperature for several hours without becoming sufficiently inelastic or hard to crack on sharp bending or to break under a sharp blow.

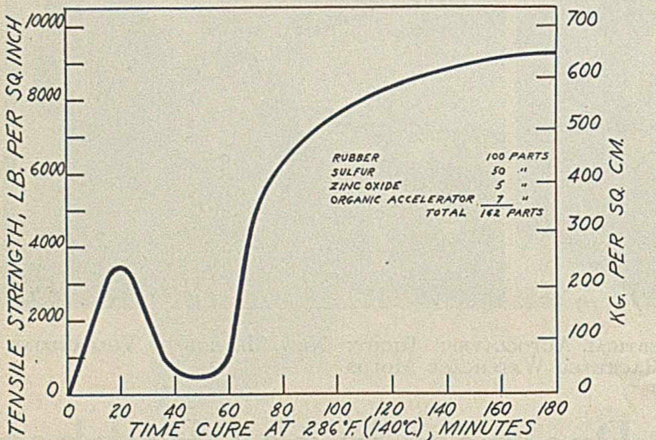


FIGURE 1. PROGRESSIVE CHANGES IN TENSILE STRENGTH WITH TIME OF CURE

Oxygen, which attacks unworked rubber but slowly, unless it is heated or exposed to direct sunlight, appears from recent investigations by Shacklock (*13*), Cotton (*4*), Busse (*3*), and others, to play the major part in the plasticization of rubber during mechanical working. It was formerly thought that the work—i. e., frictional heat—produced some sort of disaggregation or depolymerization through breaking up the cellular structure which coagulated rubber possesses. The microscope shows that the coagulation of the latex particles by formic or acetic acids (the standard coagulating agents) does not appreciably rupture the latex particles, but, through neutralization of their negative electrical charges, causes them to cohere. The mechanical theory of the breakdown process must be abandoned, for mastication of rubber in the absence of oxygen produces only slight permanent plasticization, as has been shown by conducting the process in an atmosphere of nitrogen. "Depolymerization," "cyclization," "disaggregation," or whatever you may choose to call it, of the molecular complexes may occur, but the presence of oxygen is fundamental to the physical changes. The writer has come to view the mastication of rubber as being somewhat similar in character, if not in speed, to what would occur if metallic sodium were worked between oppositely rotating mill rolls. With each exposure of fresh surface to the air, a film of oxide would flash across the surface, dulling its luster, and eventually complete conversion of the metal into sodium oxide (or hydroxide in the presence of moisture) would result. In the case of rubber the action is extremely slow, but long continued milling in air converts crude rubber into a sticky, oxidized, semifluid mass, unmanageable on mixing rolls. As regards the amount of oxygen that would be taken up in the two cases, the analogy fails, for, in the case of one experiment with rubber cited in the literature (*4*), the excessive stickiness occurred at an increase in weight of only about 0.25 per cent, and beyond 0.3 to 0.4 per cent the rubber became unmanageable on the mill. While the increase in weight probably does not represent all the oxygen added, some probably being lost as volatile oxidation products, it does show how sensitive the physical properties of rubber are to small increments of oxygen. The difference in time factor (sodium *vs.* rubber) would be extremely great, since it required 90 minutes of milling to produce the 0.25 per cent increase in weight in the experiment mentioned.

But, to return to vulcanization, or "curing" as it is ordinarily referred to in a rubber factory! The heat treatment in the presence of sulfur, resulting in chemical combination of part of the sulfur, gives a product of much enhanced strength and elasticity and much less tendency to lose this elasticity at either high or low temperatures. The product is markedly stabilized, as compared with a mixture of similar composition which has not been vulcanized; what is lost in stability during the softening process of milling and the incorporation of pigments is more than regained after vulcanization.

The physical changes produced by vulcanization as measured by change in tensile strength are shown in Figure 1. The mix, which contains sulfur in excess of the total amount which will chemically combine (32 per cent; cf. Figure 2), passes first to the valuable soft rubber stage; then to a brittle, worthless, weak state; then, if the heating is continued, to a horny, tough, again commercially valuable product; and eventually to the hard, brittle consistency known as ebonite. Vulcanization, discovered in 1839, must still be considered the major discovery of rubber chemistry. It is the process upon which the industry is founded.

RECLAIMED RUBBER

The next important advance in rubber chemical technology occurred just before the turn of the century, when Marks (*8*) patented and commercialized his alkali process of reclaiming vulcanized rubber. Vulcanization almost completely removes the plastic properties of rubber, and until Marks's discovery it was impossible to reshape or reuse soft vulcanized rubber scrap. Inasmuch as rubber at that time was selling for approximately $1.00 a pound, a method of reusing such scrap had great economic significance, and still has under normal market conditions.[1]

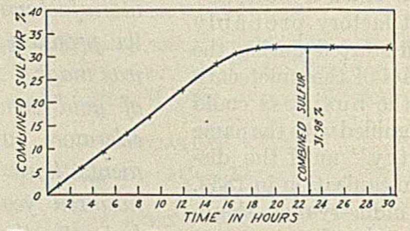


FIGURE 2. VULCANIZATION OF EXTRACTED RUBBER WITH 37 PER CENT OF SULFUR AT 135° C. (SPENCE AND YOUNG)

Through the action of high temperatures (340–370° F. or 171–188° C.) and caustic soda in the Marks process, plastic properties were again imparted to the scrap. The alkali removes the *free* sulfur, which otherwise would cause a hardening of the scrap through vulcanization to a higher state of cure, and also decomposes any cotton fabric which the scrap contains. The heat was supposed to depolymerize the rubber, converting it into a plastic condition. It is now known that oxygen (*12*) plays a large part in this process, as it does in the plasticizing of unvulcanized rubber. The process is probably both chemical and physical in nature.

---

[1] Today, with new rubber selling at prices even below 5 cents a pound, the economic importance of reclaimed rubber is considerably diminished, but it is still used in large quantities for certain purposes, owing to its processing advantages.

ACID COMPOUNDING INGREDIENTS

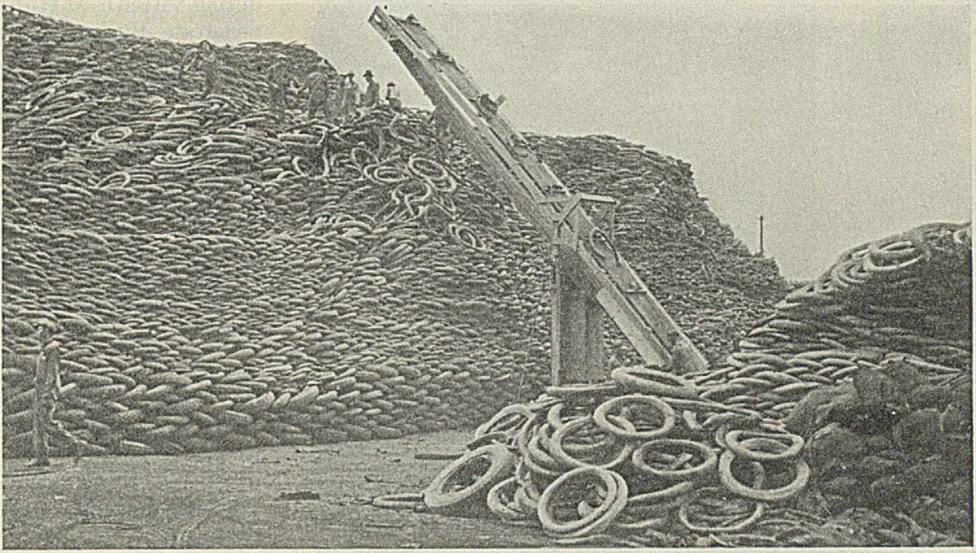
The years from 1839 to 1904 saw many important compounding advances, but no outstanding chemical discovery of technical importance need be cited. Various oils and resins came into use for softening the rubber. Oxides of calcium, magnesium, and lead were applied as accelerators. Fillers such as whiting, clays, and blanc fixe were used to stiffen the compounds and reduce costs. Zinc oxide and certain clays were found to reënforce the rubber.

The year 1904 saw the introduction by Weber (*16*) of acid materials (specifically, oleic acid) for improving the curing properties of low grade rubbers, which are deficient in naturally occurring acids and hence are slow-curing. Just why acids caused improvement was not known at that time. Many years elapsed before acids became accepted compounding ingredients. Perhaps this was due to the rapidly increasing use of high grade plantation rubber, which ordinarily contains sufficient acid materials for satisfactory vulcanization. We now believe that these acids function through dissolving the zinc or other basic oxides present (forming in the case of zinc oxide and stearic acid, for example, zinc stearate, which is soluble in rubber and has a marked effect on both the curing rate and the resulting physical properties). It is now known that amounts of acid far in excess of those occurring naturally in high grade rubber are advantageous from the standpoint of softening the rubber, dispersing the pigments and increasing the quality of the matrix. Stearic acid, lauric acid (from coconut oil), and free organic acids (usually of the fatty series and of high molecular weight) from many other sources are used regularly in the compounding of rubber mixes, hardly a recipe failing to contain some such ingredient.

ORGANIC ACCELERATORS

A new epoch in the history of the rubber industry began in 1906, when Oenslager (*6*) discovered the first organic accelerator of vulcanization. Vulcanization, in the presence of sulfur alone, is a slow process, 2 to 3 hours of heating at 40 pounds per square inch (2.8 kg. per sq. cm.) steam pressure (287° F. or 142° C.) being required to produce the soft rubber stage. Catalysts of the process were as old as vulcanization itself, white lead being present in the mixture with which Goodyear made his discovery of the process. Lime, litharge, and magnesia were soon found to speed up the reaction, and became regularly used in fabricating rubber goods. The introduction of organic substances in their place produced goods of remarkably enhanced physical properties, and in a fraction of the time of heating.

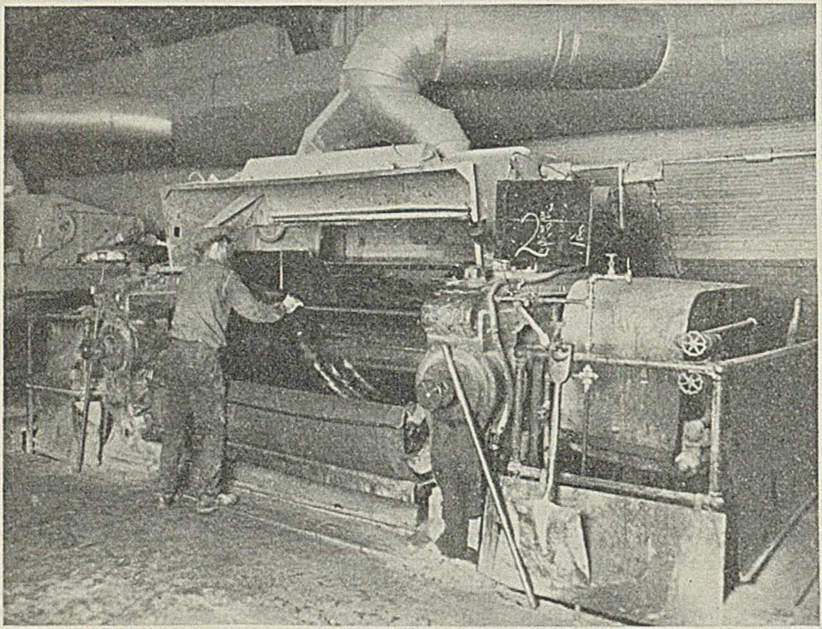
The history of this discovery is an interesting story. Rubber from the *Hevea brasiliensis* tree was selling at a high figure. Cheaper substitutes were being investigated, and it was found that a cheaper resinous rubber, known as Pontianac, offered possibilities, provided it was deresinated. Such deresinated rubber was quite firm, but it would not vulcanize like Hevea rubber. Oenslager found that aniline removed this objectionable characteristic and permitted blending of this deresinated Pontianac with Hevea, with marked savings. Then it developed that aniline enhanced the properties of vulcanized Hevea itself and shortened the period required for its vulcanization. Other materials were soon found by Oenslager and others, until now we have available a long list of organic substances which accelerate the vulcanization process. Aniline was volatile and toxic. These objectionable characteristics were removed by "fixing" it by means of carbon disulfide or formaldehyde. Thiocarbanilide and methylene aniline thus replaced aniline. Thiocarbanilide has certain objectionable characteristics, causing, among other things, premature vulcanization during the mixing and processing stages. It occurred to Bedford (*2*) that this and other nitrogenous substances which showed accelerating properties were not the actual accelerating materials, but probably reacted with sulfur during the vulcanization process. Therefore, he heated thiocarbanilide with sulfur outside of rubber and obtained a resinous product of enhanced value. Unawares he had synthesized mercaptobenzothiazole, which in its purified form constitutes one of the major organic accelerators used today.



WORN-OUT TIRES TO BE DEVULCANIZED

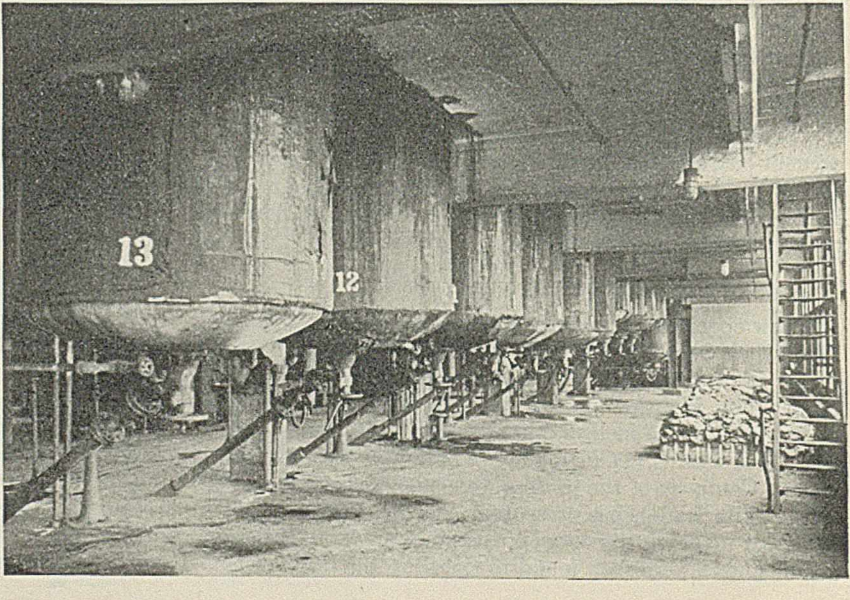
The commercial value of these organic accelerators to the rubber industry can hardly be overestimated. Curing time has been reduced from one-half to one-third that formerly required, with tremendous savings in molding equipment. In the case of certain thin articles as, for example, inner tubes, the curing time has been cut to one-tenth that formerly required. In fact, certain accelerators, such as the thiuram monosulfides, thiuram disulfides, and the dithiocarbamates, permit the compounding of mixtures which will cure in a few minutes at 40 pounds steam pressure, or, in the case of the last named group, will cure spontaneously at ordinary tempera-

tures in a few days. The time factor in curing is limited only by the thickness of the article to be molded and the temperatures developed during the processes of mixing, calendering into sheets, or extruding into the desired shape. The heat conductivity of rubber is low, and that of rubber-fabric combinations still lower, so that considerable time must be allowed during vulcanization for the heat to penetrate thick articles. The mixing mills develop, even with efficient cooling, temperatures close to that of boiling water, so that many of the active organic accelerators cannot be applied where a milling process must be used, as premature vulcanization or scorching occurs while the article is being formed. However, such accelerators find application in latex mixtures or in rubber cements where heat is not involved in the processing steps.



Reënforcement

During the years from 1912 to 1915, when the industry was hard-pressed to produce better-wearing tread stocks to meet the demands of the automotive industry, the introduction of gas black as a pigment for reënforcing rubber occurred. Up to that time zinc oxide had been the only pigment which had marked reënforcing properties. The shortage of this pigment at that time, together with its relatively high volume cost, stimulated search for a new reënforcing agent. Again, Oenslager (*14*) receives the credit for a major advance in the industry. His work on gas black, together with that on organic accelerators, is shortly to be recognized by the American Section of the Society of Chemical Industry in the award of the Perkin Medal. Oenslager increased the concentration of gas black, which previously had been used only in



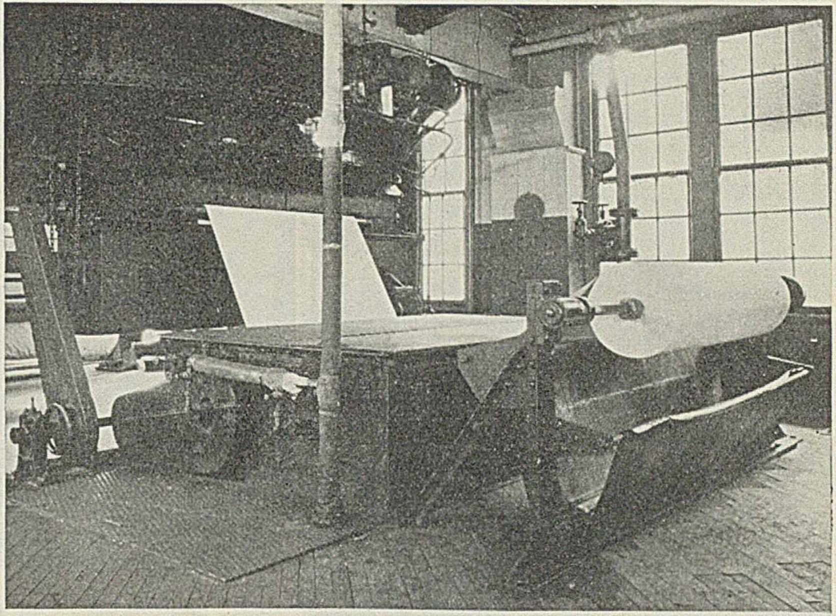
Upper: Crude Rubber (Smoked Sheets in Bales)

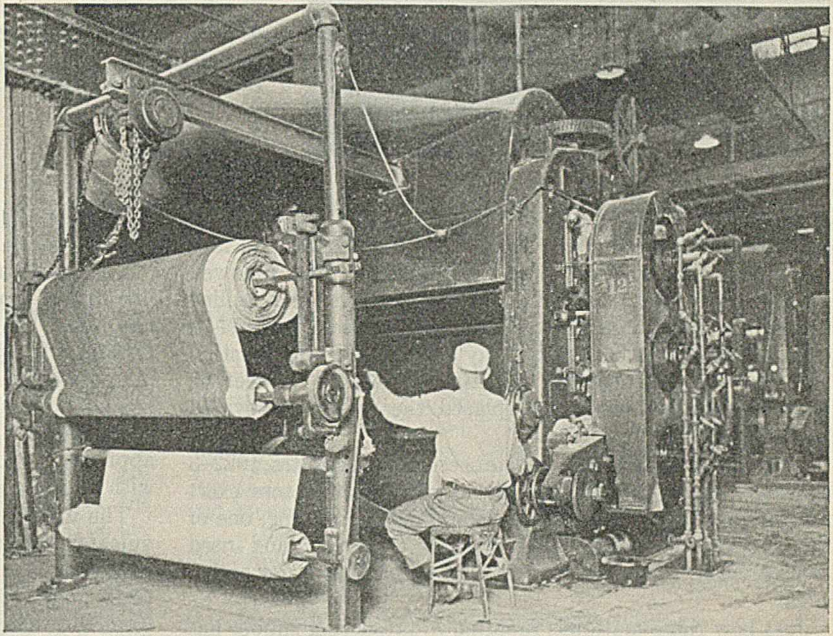
Center: Mixing Tire Tread Stock on 84-Inch Mill

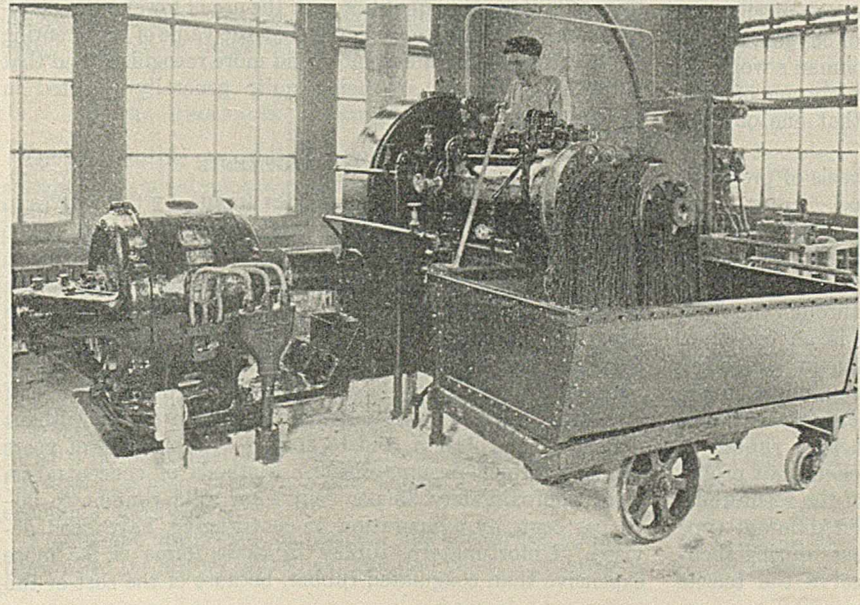
Right: Battery of Vertical Autoclaves for Reclaiming Rubber Scrap low concentrations and chiefly to color rubber mixes black. He found that this move resulted in marked improvement in abrasion resistance and the wear of tire treads. Strangely enough, full advantage of this valuable compounding ingredient was not taken for more than a decade. This was probably due in part to the difficulty of incorporating black with rubber. Batches containing a high volume of black develop a high temperature during milling, and there were many problems to be worked out in properly dispersing the black. Again, because of its high adsorptive power, gas black retarded cure, and new organic-accelerator combinations had to be developed for use with carbon black. Also, there was an aging problem, as gas black compounds did not age as well as those compounded with zinc oxide.

Antioxidants

The discovery of antioxidants for rubber marked the next outstanding discovery in the rubber industry. It solved, to a large extent, the aging problem with gas black compounds, as well as with rubber compounds in general. It was the logical next step in advancing rubber technology. Discovery of some such material was a vital necessity in the case of the German synthetic rubber, on account of its poor keeping qualities, and as early as 1918 (*1*) phenolic bodies for retarding the oxidation of such synthetic products were covered by patent. With the possibilities further emphasized by the stimulating researches of Moureu and Dufraisse (*10*), the discovery of an "antioxygen," "anti-ager," or "antioxidant" for rubber became the objective of most of the large rubber-research laboratories. Just when the use of such materials was initiated, the writer does not definitely know. Work was in progress during 1922, and the date



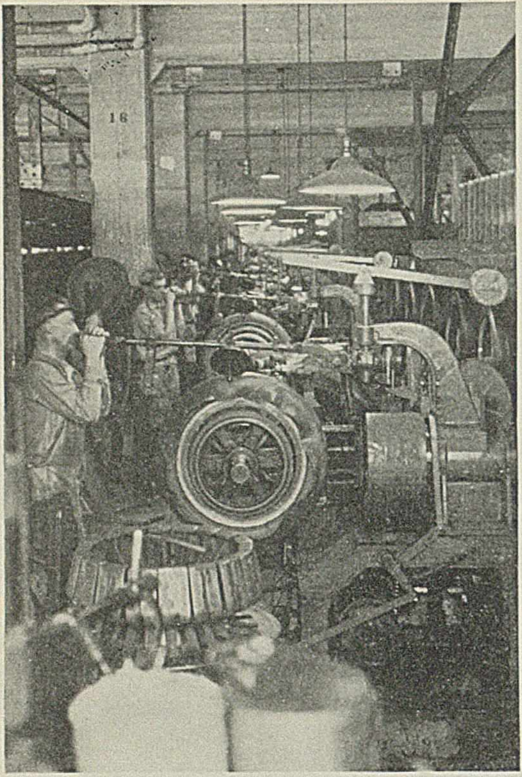


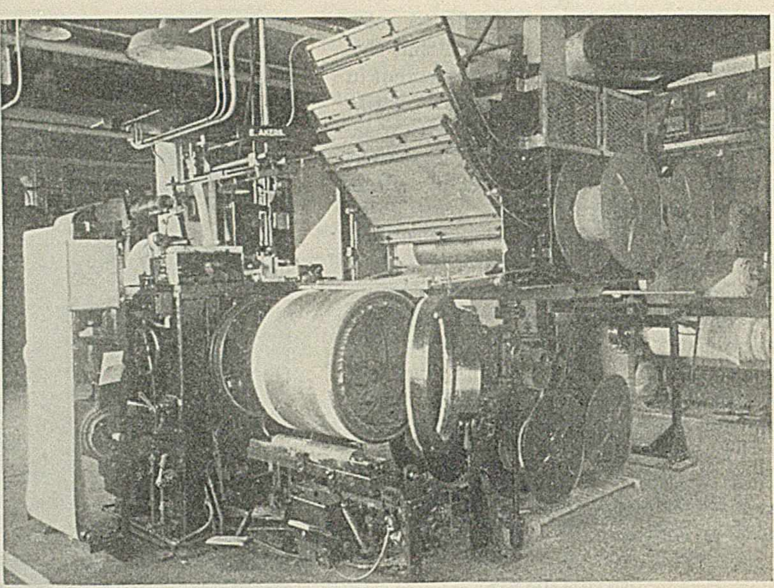


Upper: Cord Fabric Entering Equipment for Impregnating with Rubber Cement

Center: Coating Impregnated Cord Fabric with Compounded Rubber on Calender

Left: Straining Reclaimed Rubber to Remove Metallic and Other Foreign Materials





Above: New Method of Building Pneumatic Tires on Drum

Left: Former Method of Building Pneumatic Tires on Core

of the patent application of Winkelmann and Gray (*17*) on aldol-α-naphthylamine was April, 1923. This was the first antioxidant for rubber to be marketed. It was followed shortly by a reaction product of acetaldehyde and aniline formed in acid solution. At the present time, phenyl-α-naphthylamine, phenyl-β-naphthylamine, and the reaction products of acetone with diphenylamine, and of acetone with aniline have largely displaced the earlier discovered antioxidants.

The use of antioxidant substances really predates 1922–3 by many years, as many of the organic accelerators exert marked antioxidant action. *p*-Aminodimethylaniline, one of the accelerators early discovered by Oenslager and used commercially for many years, has a marked preservative effect.

Just how these materials function in preserving rubber has been a matter of much speculation. Whether the mechanism is one of selective or preferential absorption of oxygen, or of a negative catalytic effect, is not settled. Kohman's work (*7*) indicates that the action, in certain cases, is not one of preferential absorption, but the writer believes that one or both mechanisms are involved in many cases.

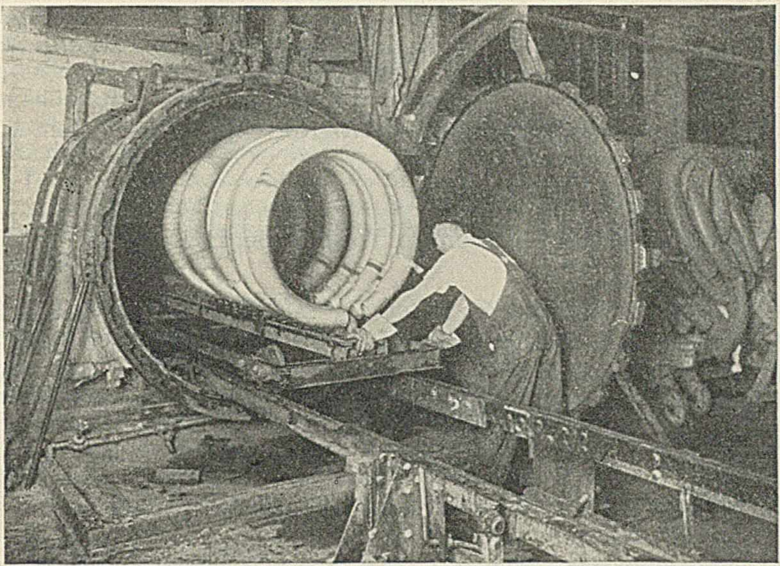
Antioxidants were first evaluated on the basis of preservation of tensile strength after an aging period. Later it became evident that they differed widely in their effect on the tendency of vulcanized rubber compounds to crack on flexing. This effect is observable in freshly cured rubber samples which have not been aged at all. It is now known through the work of Neal and Northam (*11*) that cracking is an oxidation phenomenon; hence antioxidants are of value in preventing cracking. From unpublished experiments conducted in the writer's laboratory, it is evident that some organic materials which reduce the tendency of highly pigmented rubber to crack, function not through an antioxidant effect, but probably through an influence on the dispersion of the reënforcing pigment. Also, it appears to be a somewhat different type of oxidation from that which ordinarily occurs during shelf-aging, for certain antioxidants which preserve the tensile properties of a rubber compound have little or no beneficial effect upon its resistance to flex-cracking.

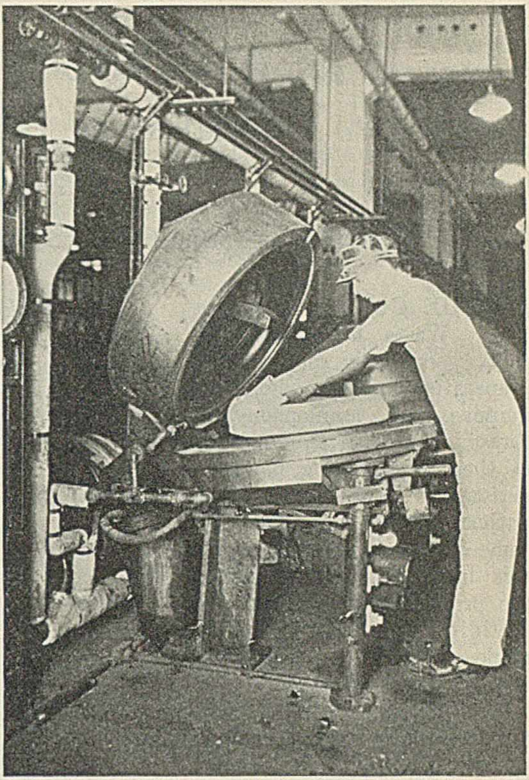
The importance of antioxidants to the rubber industry is, like that of organic accelerators, hard to overstate. Geer (*5*) has given the opinion that rubber goods containing antioxidants, if properly compounded and cured, will suffer no more deterioration in ten years of shelf-aging than a similar compound containing no antioxidant will suffer in one year. Also, their use, through preventing flex-cracking, permits the application of considerably higher concentrations of gas black, with consequent improvement in wear resistance.

The influence of curing temperature on the quality of the vulcanizate has recently received much attention. Many technologists had expressed the opinion that lower temperatures were productive of higher quality. Recently, work from the writer's laboratory (*15*) has shown a definite trend toward better aging qualities with the use of lower curing temperatures. The writer believes that the value of lower curing temperatures is becoming more and more recognized and that lower temperatures are being quite generally adopted in the industry.

Latex Developments

The very earliest rubber articles (made by the natives in those countries where rubber trees grew wild) were made through evaporating latex. Because of the difficulties due to spontaneous coagulation of latex in transit, direct application of latex failed to materialize, either on the continent or in America, when the manufacture of rubber goods in these countries was begun. In recent years, however, satisfactory methods of preserving latex, especially through the use of ammonia, have made it possible to transport latex without danger of coagulation, and to keep it over a period of years without serious decomposition. Methods of concentration from approximately 35 per cent total solid content to 60–70 per cent, by evaporation or centrifuging, have been devised. Unfortunately, rubber in these forms is far more expensive than coagulated rubber, because of the cost of the





Above: Former Method of Vulcanizing Inner Tubes in Open Steam in Horizontal Autoclave

Right: New Method of Vulcanizing Inner Tubes in Steam-Jacketed Individual Mold

preservative, increased freight costs due to the volume of water which must be transported along with the rubber, or processing costs of concentration. This has had a serious effect on the commercial application of latex. In 1931 only approximately one per cent of the rubber imported into America was in the form of latex. Its present use is limited chiefly to the rubberizing of fabrics; the production of thin rubber goods, such as surgeons' gloves, either by dipping or by electrodeposition (the Anode process); coating of grids, screens, and irregularly shaped metal objects difficult to fabricate by ordinary methods (by electrodeposition); the preparation of adhesive cements, carpet cements, and the manufacture of certain sponge rubber products (*9*). The use is increasing, however, in spite of the price differential, and the writer predicts a considerable expansion in the use of latex when the percentage price differential decreases, as it will when the price of coagulated rubber returns to a more nearly normal figure, and the price of latex is reduced through better methods of preservation and handling.

Future Prospects in Rubber Technology

Let no scientific man shun the field of rubber technology as a branch of applied science in which most of the problems have been solved. Great as the advances have been in the past century, those who have spent many years in rubber technical work will agree that we have only scratched the surface of the possibilities in this field of research. We have little exact knowledge of the fundamental facts underlying the process of vulcanization, or the chemical and physical nature of rubber itself. Acceleration and antioxidation are little understood. It has been estimated that by present methods of incorporation only a fraction of the available surface energy of gas black is being utilized in actual reënforcement of the rubber. Cheaper and more rapid methods of plasticizing rubber are economic necessities.

Predictions are always dangerous, but the writer believes that, when the history of the next hundred years of progress in rubber technology is written, the accomplishments of the first century, significant as they have been, will be far outshone.

Literature Cited

(1) Badische Anilin- und Sodafabrik, German Patent 330,741 (1920).
(2) Bedford, C. W., U. S. Patent 1,371,662 (1921).
(3) Busse, W. F., Ind. Eng. Chem., 24, 140 (1932).
(4) Cotton, F. H., *Inst. Rubber Ind. Trans.*, 6, 487 (1931).
(5) Geer, W. C., Ind. Eng. Chem., 19, 1095 (1927).
(6) Geer, W. C., and Bedford, C. W., *Ibid.*, 17, 393 (1925).
(7) Kohman, G. T., *J. Phys. Chem.*, 33, 226 (1929); *Rubber Chem. Tech.*, 2, 390 (1929).
(8) Marks, A. H., U. S. Patent 635,141 (1899).
(9) Morris, V. N., and Greenup, H. W., Ind. Eng. Chem., 24, 755 (1932).
(10) Moureu, C., and Dufraisse, C., *Compt. rend.*, 174, 258 (1922).
(11) Neal, A. M., and Northam, A. J., Ind. Eng. Chem., 23, 1449 (1931).
(12) Sebrell, L. B., Canadian Patent 289,290 (1929).
(13) Shacklock, C. W., *Inst. Rubber Ind. Trans.*, 6, 259 (1930).
(14) Shepard, N. A., "Carbon Black in the Rubber Industry," in J. Alexander's "Colloid Chemistry," Vol. IV, p. 310, Chemical Catalog, 1932.
(15) Shepard, N. A., and Street, J. N., Ind. Eng. Chem., 24, 574 (1932).
(16) Weber, L. E., "Chemistry of Rubber Manufacture," p. 241 (footnote), Ch. Griffin & Co., London, 1926.
(17) Winkelmann, H. A., and Gray, H., U. S. Patent 1,515,642 (1924).

Received October 26, 1932. Presented before the Lehigh Valley Section of the American Chemical Society, Palmerton, Pa., October 21, 1932.

Lithuania Considers Replacing Benzine with Spirits as Automotive Fuel. The Lithuanian Government is conducting experiments in the use of spirits made from cellulose for motor fuel with the intention of making their use obligatory in place of benzine, according to a report from the Consulate at Kovno, Lithuania, made public by the Commerce Department. It is stated that a committee of the Ministry of National Defense has been successful in experiments to use such spirits as fuel for automotive vehicles.

A total of 6533 metric tons of benzine was imported into Lithuania in 1931. The United States supplied 2901 tons and Soviet Russia sold 1980 tons to this market.

Amination by Ammonolysis

I. Properties and Reactions of Aqueous Ammonia System

P. H. Groggins and A. J. Stirton
Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

Ammonolysis is best interpreted as being brought about by the activity of ammonia and not by the base ammonium hydroxide. A small quantity of water catalyzes the reaction between ammonia and aromatic halides. Colorimetric studies in sealed glass tubes appear to indicate that ammonia combines with water above the critical temperature of ammonia, forming the ionogen ammonium hydroxide. The pH of aqueous ammonia decreases with rising temperature and more rapidly under such conditions when ammonium salts are introduced.

Ammonolysis with aqueous ammonia is shown to take place in the liquid phase. This fact makes it important to operate with a minimum of freeboard in the pressure system. Increased concentrations of ammonia favor the formation of a purer amine at lower operating temperatures.

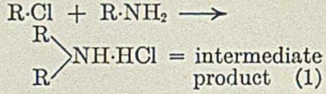
THE Color and Farm Waste Division has previously reported the preparation of 2-aminoanthraquinone and aminophenylanthraquinones by ammonolysis of the corresponding halogeno derivatives (*3–5*). One of the authors (*2*) has also discussed some of the factors involved in this unit process. Some of the problems submitted to this division by industries have made a further investigation of this process advisable.

The preparation of 2-aminoanthraquinone was selected as the principal study on account of its industrial importance and because of the fact that it is most desirable, if not entirely necessary, to obtain it directly as a product of high purity. Unlike aniline, 2-aminoanthraquinone cannot be purified by distillation and thus separated from copper compounds, hydroxy derivatives, and secondary amines. Unlike *p*-nitroaniline, it cannot be filtered under pressure in aqueous solution and then allowed to crystallize slowly in order to obtain a product of high purity.

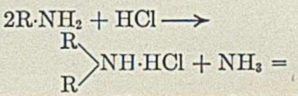
Although aqueous ammonia is generally employed in the amination of aromatic compounds, it is known that anhydrous ammonia can also be used for this purpose. When anhydrous ammonia is used, it is necessary in liquid phase operations to incorporate an organic solvent, such as an alcohol, so that ammonolysis is in reality effected with a solution of ammonia in a comparatively inert solvent. As will be shown later, when water is used as a solvent for ammonia, ammonolysis should be interpreted as being brought about by the activity of ammonia, and not by the base ammonium hydroxide. In fact, the presence of hydroxyl ions, which is due to the small concentration of dissociated ammonium hydroxide, arylammonium hydroxide, or water, is responsible for the simultaneous formation of hydroxy compounds by hydrolysis. Thus, in the preparation of aniline and aminoanthraquinones by this unit process, phenol and hydroxyanthraquinones, respectively, are found accompanying the amino compound in the reaction product.

The presence of hydroxyl ions must not always be considered deleterious. In some technical operations involving the ammonolysis of halogeno compounds, the hydroxyl-ion concentration is purposely increased in order to hydrolyze some of the ammonium halide or arylammonium halide formed during the reaction. The decomposition of such reaction products is believed to account for the acceleration in the rate and the degree of conversion of the halogen compound. Furthermore, the formation of secondary amines by condensation in the presence of ammonium halide is inhibited.[1]

The reactions relating to the formation of secondary amines are as follows:



$$R{\cdot}Cl + R{\cdot}NH_2 \longrightarrow \begin{matrix}R\\R\end{matrix}\!\!>\!NH{\cdot}HCl = \text{intermediate product} \quad (1)$$



$$2R{\cdot}NH_2 + HCl \longrightarrow \begin{matrix}R\\R\end{matrix}\!\!>\!NH{\cdot}HCl + NH_3 = \text{equilibrium product} \quad (2)$$

The first equation represents Ullmann's interpretation (*11*), the formation of the diarylamine being an intermediate step in the preparation of primary amines. According to Williams (*12*) there is present during the ammonolysis of halogeno compounds a practically definite quantity of the secondary amine, depending on the conditions employed. By reintroducing this intermediate product in subsequent charges, its further formation is inhibited. This is probably explained by the reversible character of Equation 2, which does not go to completion even when precautions are taken to remove continuously the liberated ammonia. Equation 2 shows the formation of the diarylamine as a condensation product brought about by the catalytic activity of hydrogen chloride. This is in accordance with the familiar process for making diphenylamine. The extent of diarylamine formation during ammonolysis will depend, of course, on the proportionate activity of the acid compared with the activity of ammonia and water. As will be shown later, the concentration of hydrogen chloride or its addition compounds at the close of ammonolysis is of considerable magnitude—much greater, in fact, than that ordinarily employed for the preparation of secondary amines.

The reactions involved in the formation and decomposition of the ammonium halide may be represented by the following equations:

$$R{\cdot}Cl + NH_3 \longrightarrow R{\cdot}NH_3Cl \quad (3a)$$

$$\text{or} \quad R{\cdot}Cl + 2NH_3 \longrightarrow R{\cdot}NH_2 + NH_4Cl \quad (3b)$$

$$NH_4^+ + Cl^- + M^+ + OH^- \longrightarrow NH_3 + MCl + H_2O \quad (4)$$

$$R{\cdot}Cl + M^+ + OH^- \longrightarrow R{\cdot}OH + MCl \quad (5)$$

where M can be copper or an alkaline earth.

It is obvious from the preceding equations that the reaction between ammonium chloride and a compound introducing hydroxyl ions will cause the conversion of the halogen compound to take place more completely, but the products of reaction will show a distinct increase in the quantity of hydroxy compound and a diminution in the yield or purity of the amino derivative. When the product of hydrolysis

---

[1] The presence of 2,2′-dianthraquinonylamine is here assumed from analogy with the known formation of secondary amines in the preparation of aniline, *p*-nitroaniline, *β*-naphthylamine, etc

has a value comparable to the product of ammonolysis, there is no serious objection to the employment of compounds which introduce hydroxyl ions. In the preparation of aniline the concomitant formation of phenol is not always objectionable; the situation is entirely different in the preparation of 2-aminoanthraquinone.

To obtain the best results in the amination process, it is necessary, therefore, to provide a system which is continuously neutral and in which the activity of ammonia is practically the sole activity.

pH of Aqueous Ammonia Solutions

It is of considerable importance to trace the causes contributing to the formation of hydroxy derivatives and secondary amines in the ammonolysis of halogeno compounds. Some knowledge of the change in alkalinity of aqueous ammonia with change in temperature and ammonium chloride content is therefore obviously necessary in order to make provisions leading to the inhibition of such deleterious side reactions.

Colorimetric measurements of pH appeared to be the most practical, since an opportunity was afforded to simulate temperature and pressure conditions of actual aminations by carrying out the experiments in sealed glass tubes. At room temperatures it was found that the c. p. 28 per cent aqueous ammonia used in this investigation gave a pH of 11.8, using the indicator parazo orange. When 0.027 gram of ammonium chloride was added to 1 cc. of ammonia (equivalent to ammonium chloride formed in the ammonolysis of 42.5-gram charges of 2-chloroanthraquinone), the pH was found to be only 10.7. These control experiments are important in interpreting the results obtained in the following high-temperature studies.

Change in pH with Rising Temperature. The glass tubes employed for the colorimetric studies were of Pyrex glass, 20 cm. long, external diameter 7 mm., internal diameter 5 mm. These were completely immersed in a bath of liquid petrolatum, after having been filled with approximately 1 cc. of solution, and sealed. A thermometer was suspended in the bath, and observations of the color of the solution were made as heating progressed.

The Pyrex glass employed was resistant to water as a solvent, as was evident when neither aqueous solutions of thymol blue (transition interval 8.2 to 9.2 at 100° C.) or bromothymol blue (transition interval 6.0 to 7.6) changed in color when the temperature of the bath became as high as 180° C. There is, however, the possibility that aqueous ammonia would exert a greater solvent action on glass under these conditions. For this reason the pH value at 180° C. may indicate a greater alkalinity than that which may be due to the aqueous ammonia solution alone at that temperature, and accordingly it is best to consider the pH values as comparative rather than actual.

In investigating the pH of aqueous ammonia solution at elevated temperatures, it was necessary first of all to eliminate those indicators which suffered a permanent color change on heating. With this criterion in mind it was found that the indicators marked (*a*) in Table I were unsuitable, since the color of the aqueous ammonia solution of the indicator changed gradually during heating to 130° C., and, on cooling, the original color did not return.

The phthalein and sulfonphthalein indicators are soluble in 28 per cent ammonia, and in all of the experiments it was found convenient to use an ammoniacal solution in which the indicator was present to the amount of 0.005 per cent, since at this concentration the change in color of the solution was readily observed.

When the ammoniacal solution of the indicator thymolphthalein was investigated, it was observed that the blue color became paler as heating continued and was colorless at 150° C. On cooling the tube, the solution became blue again. The blue hue was, however, paler than the original solution of the indicator before heating, showing that some actual destruction of the indicator had occurred. Some permanent fading of the indicator under such conditions is to be expected, since alkaline solutions of thymolphthalein fade gradually even at room temperature.

A tube prepared as above but containing in addition ammonium chloride in the concentration formed in ammonolysis (7/40 mole in 315 grams 28 per cent aqueous ammonia) was observed to become colorless at 85° C., indicating a pH of 8.7. Upon cooling, the blue color reappeared and was only slightly paler than the original color. As might be expected, the experiments in which thymolphthalein was used as the indicator therefore show: (1) that the pH of the aqueous ammonia decreases with increase in temperature; and (2) the decrease in the pH of aqueous ammonia is more rapid when ammonium chloride is added.

Table I. Indicators Investigated in Sealed Tube Experiments

Indicators	pH Room temp.	pH 100° C.	Color Change
Neutral red[a]	6.8–8.0	.....	Red–yellow
Phenolsulfonphthalein[a]	6.8–8.4	7.3–8.3	Yellow–red
o-Cresolsulfonphthalein[a]	7.2–8.8	7.6–8.8	Yellow–red
m-Cresolsulfonphthalein	7.6–9.2	.....	Yellow–purple
Thymolsulfonphthalein	8.0–9.6	8.2–9.2	Yellow–blue
o-Cresolphthalein[a]	8.2–9.8	.....	Colorless–red
Phenolphthalein[a]	8.3–10.0	8.1–9.0	Colorless–pink
Thymolphthalein	9.3–10.5	8.7–9.5	Colorless–blue

[a] Unsuitable indicators.

For information on the behavior of the aqueous ammonia system at temperatures somewhat nearer the temperature of effective ammonolysis, it was necessary to investigate the use of an indicator having a less alkaline range. Thymolsulfonphthalein (thymol blue) proved to be a useful indicator for this purpose. At about 160° C. and above, there is evidence that partial destruction of the indicator begins, although this destruction is not complete and permanent unless the solution of the indicator is heated for an hour at 180° C. The solution then becomes red, and remains red on cooling, indicating that some permanent chemical transformation has occurred. However, if those tubes in which a color change from the blue to the yellow has been noted are withdrawn promptly and cooled, the original color is observed to return in entirety. The indicator is therefore suitable for temperatures up to 160° C.

In a tube containing only the ammoniacal solution of the indicator, the color of the solution faded gradually as heating progressed and became yellow at 175° C. This fact would indicate that aqueous ammonia at 175° C. has a pH of about 8.2. When the reagent ammonia was substituted by an ammonia solution of equal strength prepared by bubbling ammonia into distilled water free from carbon dioxide, the results obtained in the sealed tube experiments were the same. When ammonium chloride was present in the ammoniacal solution of the indicator in the concentration previously mentioned, the solution changed color very gradually as heating progressed, and became yellow at 120° C. On cooling rapidly from this temperature, the solution regained its original blue color. Various ammonium salts besides ammonium chloride were found to behave similarly in the sealed tube experiments.

Several experiments in which the ratio of free space to liquid was varied proved that this had no appreciable influence on the temperature at which the color change took place. Control experiments in which the ammonium chloride was substituted by sodium chloride and by potassium chlorate behaved like ammoniacal solutions of the indicator alone.

Various indicators having a slightly smaller alkaline range than thymol blue were tried in an attempt to ascertain the effect of the ammonium salt at the temperatures of ammonolysis (180–200° C.). In all cases, owing to the rapid fading of the indicator at these temperatures, no color changes were observed which could be attributed definitely to the suppression of the hydroxyl-ion concentration.

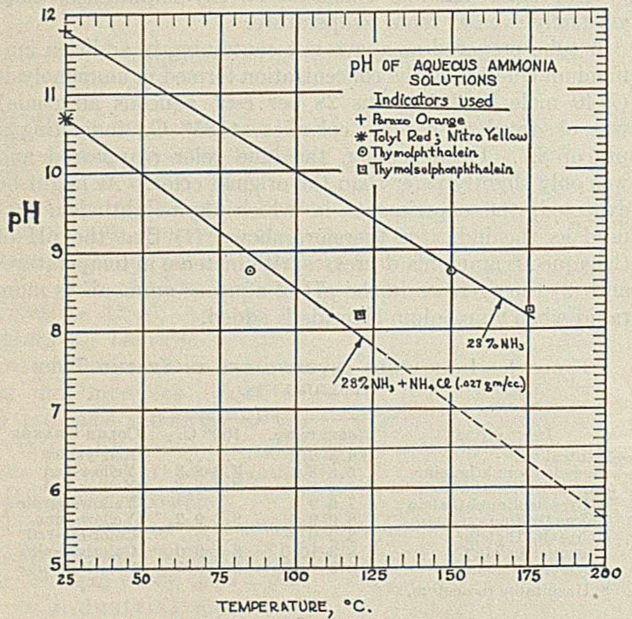


FIGURE 1

DISCUSSION. The ionization constant, K_{H_2O}, increases with increase in temperature. The ionization product of water, P_{H_2O}, will therefore decrease with increase in temperature, as will, accordingly, the pH of neutrality. The transition interval of most indicators is appreciably affected by the increasing ionization of water, indicators of alkaline range having transition intervals in a smaller alkaline range as the temperature of the aqueous solution increases. The sulfonphthaleins alone have almost unchanged sensitivity for hydrogen ions as the temperature is changed from 18° to 100° C. (*8*).

Assuming that aqueous ammonia (like water) does not appreciably attack the Pyrex glass tubes at 160–180° C. (thus introducing alkali), and assuming further that there is no significant departure at temperatures greater than 100° C. from the transition interval as determined at 100° C. for the indicators used, it is evident from the preceding sealed tube experiments that 28 per cent aqueous ammonia has a pH of about 8.7 at 150° C., and at 175° the pH is apparently 8.2, since thymolsulfonphthalein changes from blue to yellow at this temperature. The corresponding values for neutrality at these temperatures are pH 5.8 and 5.7, respectively. In those experiments in which ammonium chloride was present in the ammoniacal solution and which correspond to actual conditions during ammonolysis, the indicated pH at 120° C. was 8.2, which is greater than the corresponding pH of neutrality—i. e., 6.0. If no ammonium hydroxide is present in solution, a pH of less than 6 is to be expected, since the solution would then be faintly acid because of the hydrolysis of the ammonium salt. If the curve relating to ammoniacal ammonium chloride solutions (Figure 1) is extrapolated, it is apparent that at 200° C. the indicated pH would be approximately 5.6, the pH of neutrality.

The curves in Figure 1 show qualitatively the downward trend of the pH with increasing temperatures. Owing to the possibility of introducing alkalinity into the system by the attack of aqueous ammonia on the glass tube, and because of the probability that the transition interval of the indicator is really lower at 120–180° than at 100° C., there is reason to believe that the true pH of the solutions is closer to neutrality than is indicated in the curves.

An attempt was made to determine whether the value pH 8.2 might have been due to alkalinity derived from the glass at 175° C. Concentrated aqueous ammonia was heated to 175° C. in the sealed Pyrex tubes, and, after cooling, the pH of the solution was again determined. The pH did not appear to differ from that of the original solution—viz., pH 11.8 at 25° C. From the following considerations it will become apparent that it is not feasible to settle this question by such means.

The pH of 11.8 at 25° C. corresponds to a hydroxyl-ion concentration of 0.00631 at 25° C. The pH observed at 175° C. (8.2) corresponds to a hydroxyl-ion concentration of 0.0000316 at 25° C. Assuming that the observed pH or deviation from true neutrality is due to the alkalinity introduced by attack on glass, we have:

$$\begin{array}{lr}
(\mathrm{OH^-})\ \text{aqueous ammonia at 25° C.} & = 0.00631 \\
(\mathrm{OH^-})\ \text{glass} & = 0.0000316 \\
\hline
 & 0.0063416 = 6.342 \cdot 10^{-3}
\end{array}$$

$$\log 6.342 \cdot 10^{-3} = -2.19777 = -\mathrm{pOH}$$

$$\mathrm{pH} = 11.802, \text{ compared with } 11.8$$

The difference in the observed pH and that of the pH of neutrality at 175° C. is, therefore, 0.002 in terms of the pH of 28 per cent aqueous ammonia when determined at room temperature. It is clear that such a minute difference is not susceptible to colorimetric evaluation.

AMMONIA, THE AMINATING AGENT

The following evidence may be advanced to show that ammonia (NH_3) and not ammonium hydroxide is the aminating agent:

It is known that ammonolysis may be carried out in the vapor phase with anhydrous ammonia in the presence of metal catalysts (*1*) or in the liquid phase with anhydrous ammonia dissolved in an inert solvent (*6*).

From vapor pressure studies it has been found that the water vapor pressure closely follows the curve calculated from Raoult's law for mixtures (*13*). Furthermore, the comparative isothermal curves for the ammonia partial pressures, although showing a slight deviation from Henry's law (below the critical temperature of ammonia) also point to the same conclusion (*10*). Finally, measurements for the surface tension of water-ammonia systems reveal that these do not deviate radically from what is expected of a mixture (*7*).

Noyes and his co-workers have shown that the ionization of ammonium hydroxide, like other electrolytes, is favored by dilution and lowering of the temperature (*9*). Such conditions are not, however, favorable for the ammonolysis of aromatic compounds. Experience has demonstrated that amination proceeds best with increased ammonia concentration at elevated temperatures.

When a solution of an ammonium salt, such as ammonium chloride, is substituted for aqueous ammonia so that the concentration of ammonium ions corresponds to the concentration of ammonia that has previously been employed to advantage, it will be found that ammonolysis does not take place. The reaction mixture smells strongly of ammonia, and the product, which gives evidence of containing only a trace of amine, shows the presence of 33.9 per cent iron. This clear indication of an acid-reacting medium is entirely in harmony with the known behavior of such salts. The presence of a trace of amine is attributed to the low concentration of ammonia brought about by the hydrolysis and dissociation of the ammonium salt. Since the ammonium ions which were introduced in comparatively high concentrations did not contribute to effective ammonolysis, and since hydroxyl ions cannot possibly perform this function, it appears that ammonolysis with aqueous ammonia is similar to ammonolysis with ammonia gas dissolved in any comparatively inert solvent. Indeed, the pH studies and the review of the properties and reactions of aqueous ammonia practically compel the adoption of this viewpoint.

As ammonolysis proceeds, the concentration of ammonia diminishes, whereas that of hydrogen chloride increases. The halogen acid presumably is distributed as ammonium chloride in solution and as the salt of the newly formed amino compound. The formation of the latter addition compound appears more probable because at the temperatures of ammonolysis (150–200° C.) the amino compound, unlike ammonia, may not evidence an almost vanishing capacity to combine with water to form a base.

Function of Water in Ammonolysis

When 2-chloroanthraquinone is treated with twice its weight of anhydrous ammonia at 125–135° C., there is practically no conversion to amine. The introduction of 5 per cent by weight of water causes a slight conversion—4.9 per cent—to take place. When 30 per cent by weight of water is added, there is a diminution in the conversion to amine to 3.2 per cent. The falling off in the degree of ammonolysis upon diluting from 95 to 70 per cent aqueous ammonia would appear to indicate that the presence of a small percentage of water merely accelerates the reaction. Its function, like that of ethanol or other comparatively inert solvents, is probably that of providing a vehicle wherein a more effective contact is made between the ammonia and the compound being treated.

Comparative Ammonia and Water Vapor Pressures. When insoluble compounds having high melting points are aminated, it is important to carry out the reaction at a temperature sufficiently high to energize the organic compound to a reactive state. A prolonged heating at a temperature below the optimum does not give equally satisfactory results. Experience has demonstrated that the adverse effects are greater when the deviation from the optimum reaction temperature is 5° C. below than when it is 5° above.

It is, however, inadvisable to promote the rate of conversion by unduly elevating the reaction temperature. The increased activity of the ammonia is obviously accompanied by an increase in the kinetic energy of the water and hydrogen chloride or its addition compounds in the reaction system. Consequently, the purity and net yield of the resultant amine always suffer by excessive heating.

The effects of operating with aqueous ammonia solutions of various concentrations may be appreciated by a study of the curves (Figure 2) and the data below, which relate to the proportionality, (partial pressure of ammonia)/(partial pressure of water):

Temp.		Molal Concentration NH_3				
° *F.*	(° *C.*)	10%	20%	30%	40%	50%
100	(37.8)	3.77	11.6	32.2	79.2	173.0
150	(65.6)	2.69	7.94	20.7	47.8	98.7
200	(93.3)	1.99	5.70	14.2	31.78	62.1
250	(121.1)	1.51	4.30	10.34	21.38	34.3

From these data (*13*) it can be observed that, with increasing ammonia concentration, there is an acceleration in the increase of the ammonia partial pressure. For a definite concentration, however, the partial pressure of ammonia does not increase as rapidly as the water vapor pressure when the temperature of the solution is increased. Thus, if we plot the quotient (partial pressure of ammonia above the liquid)/(partial pressure of water above the liquid), it is found (Figure 2) that, as the temperature rises, there will be a gradual decrease in this proportionality. From this it may be predicated that there is a proportionally increased activity of water vapor at increasing temperatures. Thus, in order to obtain the best results during ammonolysis, it is advisable to employ the lowest possible temperature that produces the necessary energy intensity factor. This condition is, in a measure, realized by increasing the molal concentration of NH_3 in the ammonia employed.

Effect of Ammonia Concentration

It is necessary to distinguish between the terms "ammonia ratio" and "ammonia concentration." The first relates to the capacity factor of the system; the second to the intensity factor. Aside from economic considerations, there are no disadvantages in using a large ratio of aqueous ammonia (25 to 35 per cent ammonia solution) with respect to the compound being treated. Within reasonable limits an increase in this ratio promotes both the yield and purity of the product obtained. The larger volume of concentrated aqueous ammonia promotes solubility and therefore causes the reaction to take place more readily.

In previous publications of this laboratory it has been shown that the activity of the ammoniacal solution as an aminating agent is approximately proportional to the ammonia concentration. It should be emphasized that, in ammonolysis, solutions containing 15, 25, 40, and 60 per cent ammonia are indeed different aminating agents. Likewise in hydrolysis, equivalent quantities of K·OH are more active than $Ca(OH)_2$, and the latter in turn is more active than H·OH. Whereas hydrolysis depends on the concentration of hydroxyl ions, ammonolysis depends upon the concentration of the ammonia complex capable of supplying the corresponding negative amine radical. To the extent that the ammonia system does this, to the exclusion of side reactions, is perfect ammonolysis obtained.

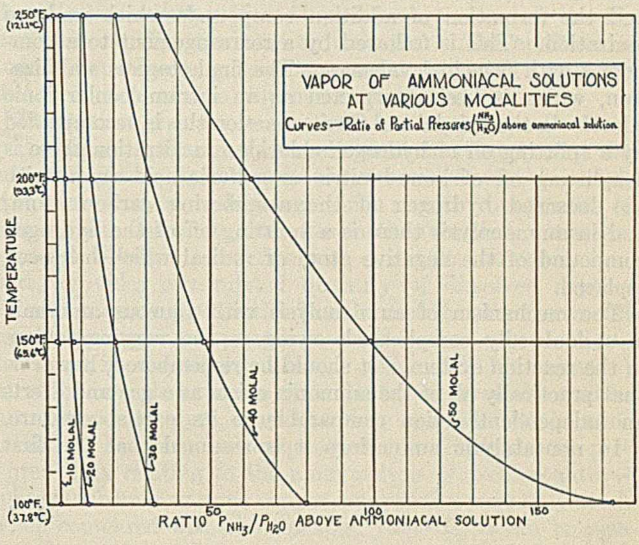


Figure 2

Extensive research has shown that the advantages to be obtained by utilizing a more concentrated ammonia solution may be summarized as follows: Amination is more rapid; conversion of reacting aromatic compound to amine is more complete; formation of hydroxy compounds is inhibited; lower reaction temperatures can be used; and, since larger batches can be treated with the same quantity of liquor, economies in the number of pieces of equipment can be effected.

Effect of Free Space in Autoclaves. Associated with the factor of ammonia concentration is the influence of "freeboard" or the free space in the autoclave. This is a matter of importance which must be taken into careful consideration in carrying out operations involving ammonolysis. When aminations are carried out in tubular systems, such tubes are filled with aqueous ammonia, and the reactants are therefore completely dissolved or wetted out. When vertical autoclaves are employed, it is essential to reproduce such conditions as closely as possible.

It is obviously advantageous to fill the autoclave up to its maximum safe capacity. Such conditions permit a larger production and generally give a better yield and purity of product. When aminations involving insoluble halides (such as halogenoanthraquinones) are carried out in glass tubes, it will be observed that the reaction takes place in the liquid phase. The solid material remaining above the surface of the liquid does not appear to react, despite the fact that it is in contact with vapors which are essentially gaseous ammonia.

When an excess of freeboard is left in the autoclaves, this space will be filled with vapors in equilibrium with the aqueous solution. The greater the free space, the greater will be the quantity of aqueous ammonia that goes from the liquid to the vapor state. Since ammonolysis of sulfonic acid and halogeno compounds takes place in the liquid phase, it is obvious that the best results can be obtained only by introducing the maximum size charge into the autoclave.

Speculation Regarding Mechanism of Reaction. The mechanism of ammonolysis appears to be identical with the usual processes involving replacement in the benzene series, whose initiation is determined by the presence of key atoms such as Cl, S, N, C=C (*14*). The necessary conditions are unsaturation in one or more of the reactants and the formation of addition compounds which undergo ionization. This is followed by a rearrangement to a compound with principal valences. The final stage is stabilization, which is best interpreted as an intramolecular ionic effect. In the Friedel and Crafts reaction this is accompanied by a splitting off of hydrogen chloride; in nitration there is a splitting off of bound nitric or sulfuric acid anion with the loosened hydrogen of the neighboring carbon atom; and in ammonolysis there is a splitting off of the hydrogen compound of the negative atom or radical which has been replaced.

The mechanism of ammonolysis with aqueous ammonia is undoubtedly complicated, owing to the varying factors in the reaction system. It should be remembered, however, that practically all of the ammonia exists as a gas and exerts an independent action comparable to its partial pressure.

In noncatalytic aminations it is assumed that the first stage is the formation of an addition complex between ammonia and the aromatic compound. The following formulations show how such solute-solvent complexes resemble the more stable addition compounds of the amines:

$$\mathrm{R{\cdot}Cl + NH_3 \longrightarrow R(NH_3)Cl \longrightarrow R{\cdot}NH_3{}^{+}{\cdot}Cl^{-}}$$
$$\mathrm{R{\cdot}OH + NH_3 \longrightarrow R(NH_3)OH \longrightarrow R{\cdot}NH_3{}^{+}{\cdot}OH^{-}}$$
$$\mathrm{R{\cdot}SO_3Na + NH_3 \longrightarrow R(NH_3)SO_3Na \longrightarrow R{\cdot}NH_3{}^{+}{\cdot}SO_3Na^{-}}$$

Since ammonia exhibits an almost vanishing capacity to form bases at increasing temperatures, it appears probable that during the reaction the liberated acid or water is largely attached to the newly formed amine. The concentration of such salts or bases determines the equilibrium of the reaction for each temperature. When the ammonia system is cooled, the power of ammonia to form the ionogen ammonium hydroxide increases, and the distribution of the hydracid (in the ammonolysis of halogens) would depend on the basicity of the amino compound.

Literature Cited

(1) Arnold, H. R., U. S. Patent 1,799,772 (1931).
(2) Groggins, P. H., *Chem. & Met. Eng.*, 36, 273 (1929).
(3) Groggins, P. H., Ind. Eng. Chem., 22, 620 (1930).
(4) Groggins, P. H., and Newton, H. P., *Ibid.*, 21, 369 (1929).
(5) Groggins, P. H., Stirton, A. J., and Newton, H. P., *Ibid.*, 23, 893 (1931).
(6) Hale, W. J., and Cheney, G. H., U. S. Patent 1,729,775 (1929).
(7) King, H. H., Hall, J. L., and Ware, G. C., *J. Am. Chem. Soc.*, 52, 5128 (1930).
(8) Kolthoff, I. M., and Furman, N. H., "Indicators," pp. 85–93, Wiley, 1926.
(9) Noyes, A. A., *Carnegie Inst. Wash. Pub.* 63 (1907).
(10) Perman, E. P., *J. Chem. Soc.*, 1901, 718.
(11) Ullmann, Enzyclopädie der technischen Chemie, Vol. I, p. 440.
(12) Williams, W. H., U. S. Patent 1,775,360 (1930).
(13) Wilson, T. A., Univ. Ill. Eng. Expt. Sta., *Bull.* 146 (1925).
(14) Wohl, A., and Wertyporoch, E., *Ber.*, 64, 1308 (1931).

* * * * *

II. Effect of Metal Catalysts in Ammonolysis

The amination of organic compounds containing replaceable substituents by treatment with aqueous ammonia is a normal one which can be accelerated by the employment of catalysts. When halogen atoms or sulfonic acid groups are to be replaced, it is best to use the compounds of metals following hydrogen in the electrochemical series. In the preparation of amines from alcohols, aldehydes, and ketones, the compounds of the more active metals are the most useful catalysts.

In the preparation of amino compounds from halogen derivatives in the anthraquinone series, there is no advantage in keeping the copper catalyts in the reduced state, or in using metallic copper along with a copper compound. Investigation has shown that it is best to employ an oxidant along with copper compounds, although the metal catalyst is not always necessary. When the halogen atom is attached to a phenyl nucleus, it is not practicable to operate without a copper compound or one of the metals following hydrogen in the electrochemical series. It has been found feasible to obtain 2-aminoanthraquinone and 4′-amino-2-phenylanthraquinone in a high state of purity by employing oxidants along with copper compounds. The addition of ammonium nitrate to copper salts increases both the yield and purity of the amine.

IN A previous publication Groggins, Stirton, and Newton (*5*) showed that compounds of metals following hydrogen in the electrochemical series—e. g., arsenic, copper, and silver—can advantageously be employed in the conversion of certain halogenoanthraquinones to amino derivatives. It was also brought out that the addition of a copper catalyst is instrumental in increasing the rate at which conversion to amine takes place. The catalytic activity of copper is here obviously that of accelerating a normal chemical reaction, for in some instances approximately equal results could be obtained by increasing the reaction temperature.

Although the more active metals—e. g., nickel, cobalt, and iron—were found deleterious in the ammonolysis of halogen derivatives, these metals certainly appear to be the most effective in the preparation of amines from hydroxy compounds as well as aliphatic aldehydes and ketones (*1*, *5*, *6*, *8–10*).

Effect of Metal Catalysts. Copper and its salts have been found to be the most effective metal catalysts in accelerating the replacement of the sulfonic acid group, or halogen atoms by ammonolysis. Their efficacy in a number of aminations has been somewhat exaggerated in the patent literature, where apparently many of the claims are inserted merely for protective purposes. This is particularly true in the amination of aromatic compounds containing a nitro group. Thus, in the conversion of *p*-nitrochlorobenzene to *p*-nitroaniline, Groggins (unpublished data) has found that the use of copper and its salts is actually detrimental. McMaster and Steiner (*7*) made the same observations in the preparation of *p*-chloro-*o*-nitroaniline from nitro-*p*-dichlorobenzene.

Copper salts do, however, make it possible to carry out a larger number of aminations under milder conditions of temperature and pressure. Experiments in sealed glass tubes with chloroanthraquinone show conclusively that amination progresses more rapidly at lower temperatures in the presence of such a catalyst, but the purity of the resultant amine is not increased by the presence of copper compounds. The use of copper or its salts to promote amination in chloro- and dichlorobenzenes, or in chlorophenylanthraquinones, is not only advantageous but practically indispensable. The conversion of these compounds to aniline, phenylenediamines, and aminophenylanthraquinones, respectively, is indeed not practical without the use of such a catalyst.

The catalytic activity of copper and its salts may be ascribed to the fact that copper-ammonia complexes are formed in which the ammonia is loosely attached in a large complex ion that reacts more readily than does gaseous ammonia. The copper, therefore, acts as a transfer agent, keeping a limited quantity of ammonia in a circumscribed state of mobility contiguous to the halogen compound being treated. Whether these complex cations actually take part in the reaction and are united to the aromatic compound even for a brief period as a ternary compound comprising aryl compound, ammonia, and metal is not positively known, but appears probable. When copper compounds are employed, the ammoniacal mother liquor and wash waters are fluorescent, a characteristic not observed in ordinary aminations. These fluorescent wash waters initially gave no test for ionic copper, but, on wet ignition with nitric acid–sulfuric acid, copper was found to be present, thus indicating copper in organic combination.

The fact that copper compounds are required only in small quantities supports the belief that copper-ammonio cations serve as cyclic catalysts, first forming addition compounds which subsequently undergo metamorphosis during the reaction.

When copper oxides are employed, the copper-ammonio hydroxides formed introduce hydroxyl ions to hydrolyze the $R{\cdot}NH_3Cl$ or NH_4Cl that is formed during ammonolysis of organic chloro compounds. By reacting with the newly formed halide, the reaction indicated in Equation 3 will be promoted:

$$Cu_2O + H_2O + 4NH_3 \longrightarrow 2Cu(NH_3)_2{}^{+}OH^{-} \qquad (1)$$

$$2CuO + 2H_2O + 8NH_3 \longrightarrow 2Cu(NH_3)_4{}^{++}(OH)_2{}^{--} \qquad (2)$$

$$R{\cdot}Cl + NH_3 \longrightarrow R{\cdot}NH_3Cl \xrightarrow{OH^-} R{\cdot}NH_3OH + Cl^- \qquad (3)$$

The presence of hydroxyl ions will, moreover, promote the formation of hydroxy derivatives. It is a notable fact, as can be observed from the tables which follow, that the introduction of a copper catalyst, particularly copper oxides, tends generally to lower the yields.

COPPER AND ITS SALTS AS CATALYSTS

Considerable discussion has taken place regarding the necessity of introducing metallic copper along with its salts to make ammonolysis go to completion. Hale and Britton (*4*), in their studies on aniline, attempt to prove that cuprous salts alone are only partly satisfactory, whereas cupric salts are practically ineffective. Such general conclusions are not justified from more comprehensive experimental evidence. It is probable that certain practical factors inherent in the ammonolysis of chlorobenzene make the presence of metallic copper, along with a cuprous salt, desirable. It can readily be demonstrated that copper in any physical form, such as gauze or pipe, can be used. When the metal is warmed in the aqueous ammonia system, it will pass into solution, readily forming cuprous-ammonio complexes. In the event that large pieces of metal are employed, the loss in weight can be ascertained. Such data show that the loss in weight of copper is less than stoichiometric, referred to the hydrogen chloride split off during ammonolysis.

When copper is heated in sealed glass tubes with aqueous ammonia above the critical temperature of ammonia, and the colorless solution then filtered from the metal, the filtrate will rapidly turn blue on oxidation. The addition of ammonium salts—e. g., ammonium chloride—will accelerate the formation of the cuprous-ammonio compound.

The action of aqueous ammonia on copper, particularly in the presence of ammonium salts, indicates clearly that the pressure system could not be constructed from this metal. It appears that any advantage which results from the use of copper, plus one of its salts, lies in the fact that the excess of metal, through interaction with ammonia and ammonium salts, provides a regulated quantity of dissolved copper. No advantage can be ascribed to the fact that the free metal keeps the copper compounds in a reduced or cuprous state, for there is abundant evidence, which will be presented later, to show that the use of oxidants,[1] either with or without a copper catalyst, is undoubtedly beneficial in the amination of halogeno anthraquinones. In Table I are presented data relating to the ammonolysis of 2-chloroanthraquinone wherein various copper compounds were employed. When compared with the controls, Table II, it can be seen that the results with copper compounds show little improvement.

TABLE I. EFFECT OF COPPER CATALYSTS IN AMMONOLYSIS OF 2-CHLOROANTHRAQUINONE[a]

EXPT.	2-CHLORO-ANTHRA-QUINONE	CATALYTIC MATERIALS	CATALYST	TEMP.	TIME	YIELD[b]	PURITY
	Grams		*Grams*	° *C.*	*Hours*	%	%
1[c]	36.375	Control	...	200	18	95.5	91.0
2	36.375	Cu_2O	2.0	200	24	93.3	87.6
3[d]	36.375	Cu powder Cu_2O	0.5 1.0	200	18	93.2	90.0
4[d]	36.375	Cu powder Cu_2O	1.0 2.0	200	24	90.8	88.0
5	42.5	Control	...	195	24	95.6	90.9
6	42.5	Cu powder	0.55	195	24	96.7	90.6
7	42.5	Cu_2O	0.60	195	24	96.0	92.5
8[d]	42.5	Cu powder Cu_2O	0.30 0.50	195	24	96.0	88.5
9[d]	48.5	Cu powder Cu_2O	0.25 0.50	195	24	97.5	87.4
10	42.5	$Cu(NO_3)_2.6H_2O$	2.37	195	24	96.0	93.0
11	42.5	$Cu(NO_3)_2.6H_2O$ H_2O_2.30 vol.	2.37 10.00	195	24	94.9	93.8
12	24.25	Cu_2O	2.16	180	30	90.7	90.0
13	24.25	Cu_2Cl_2	3.00	180	30	95.4	92.5
14	24.25	Control	...	180	30	95.5	87.8

[a] Capacity of autoclave, 500 cc.; 315 grams 28% aqueous ammonia used, except in expts. 12 and 13 where 275 grams were used; no purification steps performed in preparation of any of products.

[b] In all tables, yield per cent = (weight of product)/(weight of amine theoretically obtainable).

[c] Glass tube experiments show that the ammoniacal solution of controls becomes brown at approximately 180° C., whereas in the presence of copper compounds the brown color appears at approximately 160° C.

[d] According to Hale and Britton (*4*).

It can be seen from the preceding data, Table I, that the employment of copper compounds in the ammonolysis of

---

[1] Separate industrial and governmental applications for patents pending; foreign rights reserved.

2-chloroanthraquinone does not lead to the satisfactory results obtained with 2-bromoanthraquinone (*3*). It is also evident that the combination of metallic copper and cuprous salts is not productive of satisfactory results and that cupric nitrate is superior to copper in a reduced state. The greater efficacy of the nitrate is entirely in harmony with the improved results obtained (Tables III–V) by incorporating an oxidant such as potassium chlorate, or an ammonium salt of an oxidizing acid with the charge.

It has been found in the ammonolysis of the halogenoanthraquinones that copper chloride or nitrate functions at least as well as the oxide. It appears necessary, therefore, in those aminations which require copper, to attribute the principal beneficial effects of copper compounds either to the activity of the copper-ammonio cation or to the formation of a ternary complex comprising halogeno compound, ammonia, and copper.

TABLE II. CONTROLS IN AMMONOLYSIS OF 2-CHLOROANTHRAQUINONE[a]

EXPT.	2-CHLOROANTHRAQUINONE	TEMP.	TIME	YIELD	PURITY
	Grams	° *C.*	*Hours*	%	%
1	36.375	180	30	98.4	80.8
2	36.375	188	30	97.4	88.7
3	36.375	190	30	98.0	91.1
4	36.375	195	24	94.5	91.4
5	36.375	200	18	95.5	91.0
6	42.5	195	24	95.6	90.9
7	42.5	200	20	94.6	91.6

[a] Capacity of autoclave, 500 cc.; 315 grams 28% aqueous ammonia used; mean purity, expts. 2–6, inclusive, 91.25%.

TABLE III. EFFECT OF COPPER CATALYST IN PREPARATION OF 4′-AMINO-2-PHENYLANTHRAQUINONE

NITROBENZENE AS OXIDANT[a]

EXPT.	TIME	Cu_2Cl_2	Cu	NITROBENZENE	YIELD CRUDE	PURITY BY TITRATION	
						Crude	After recrystallization
	Hours	*Grams*	*Grams*	*Grams*	%	%	%
1	20	..	...	35	98.6	25.0	..
2	20	0.2	...	..	98.1	48.0	..
3	20	1.6	0.5	..	97.4	82.8	98.2
4	16	1.6	1.0	15	98.2	83.6	97.0
5	16	5.0	1.0	15	95.2	88.1	98.3
6	16	15.0	...	15	94.6	84.4	98.2

AMMONIUM NITRATE–POTASSIUM CHLORATE AS OXIDANT[b]

EXPT.	CATALYTIC MATERIALS	CATALYST	YIELD	PURITY
		Grams	%	%
1	NH_4NO_3 $KClO_3$	8 1	97.2	17.6
2	NH_4NO_3 $KClO_3$ Cu powder	8 1 2.66	96.1	97.8
3	NH_4NO_3 $KClO_3$ Cu_2O	8.0 1.0 3.0	95.6	97.5

[a] 4′-Chloro-2-phenylanthraquinone (m. p., 204–206° C.), 15.93 grams; 28% aqueous ammonia, 25 grams; temperature, 215° C.; capacity of autoclave, 500 cc.; product recrystallized from *o*-dichlorobenzene at approximately 70% yield.

[b] 4′-Chloro-2-phenylanthraquinone, 25 grams; time, 30 hours; temperature, 215° C.; 28% aqueous ammonia, 300 grams.

The data in Table II are of interest not only because the controls show results which compare favorably with those obtained by the use of copper, but particularly because the experiments at 190–200° C. show only a maximum divergence of 0.35 per cent from the mean purity of 91.25. It appears, therefore, that a purity of about 91.5 represents the best results obtainable under such operating conditions. It is necessary, therefore, to conclude that, owing to the concentration of arylammonium chloride, an equilibrium is established, which at lower temperatures (180–190° C.) prevents complete conversion and at higher temperatures (200–220° C.) serves only to introduce impurities in the reaction product. (Groggins and Newton (*2*) give data on aminations at 215–220° C.)

TABLE IV. EFFECT OF USING POTASSIUM CHLORATE WITH COPPER CATALYSTS IN AMMONOLYSIS OF 2-CHLOROANTHRAQUINONE[a]

EXPT.	CATALYTIC MATERIALS	CATALYST	TEMP.	TIME	YIELD	PURITY
		Grams	° *C.*	*Hours*	%	%
1	Control	..	195	24	95.6	90.6
2	Cu powder	0.55	195	24	96.7	90.6
3	Cu powder $KClO_3$	0.50 1.25	195	24	94.2	94.6
4	$Cu(NO_3)_2 \cdot 6H_2O$ $KClO_3$[b]	1.25 1.25	195	24	95.1	95.9
5	Control	..	200	20	94.6	91.6
6	Cu_2O	1.00	200	24	92.7	88.2
7	Cu_2O $KClO_3$	0.05 1.25	200	20	95.8	98.0
8	Cu_2O $KClO_3$	0.30 1.25	200	20	94.7	95.5
9	$Cu(NO_3)_2 \cdot 6H_2O$	0.40	200	20	96.3	92.8
10	$Cu(NO_3)_2 \cdot 6H_2O$ $KClO_3$	0.40 1.00	200	20	94.6	98.0
11	$Cu(NO_3)_2 \cdot 6H_2O$ $KClO_3$	0.40 1.25	200	20	96.6	97.0
12	$Cu(NO_3)_2 \cdot 6H_2O$ $KClO_3$	0.20 1.25	200	24	94.4	97.0

[a] 2-Chloroanthraquinone, 42.5 grams; 28% aqueous ammonia, 315 grams; capacity of autoclave, 500 cc.

[b] Effect of potassium chlorate alone discussed later.

TABLE V. EFFECT OF USING AMMONIUM SALTS WITH CUPROUS OXIDE IN AMMONOLYSIS OF 2-CHLOROANTHRAQUINONE[a]

EXPT.	2-CHLOROANTHRAQUINONE	CATALYTIC MATERIALS	CATALYST	TEMP.	TIME	YIELD	PURITY
	Grams		*Grams*	° *C.*	*Hours*	%	%
1	36.375	Control	..	200	18	95.5	91.0
2	36.375	NH_4NO_3	10	200	18	93.5	95.6
3	36.375	NH_4NO_3	6	200	24	95.9	94.5
4	36.375	Cu_2O	2	200	24	93.3	87.6
5	36.375	NH_4NO_3 Cu_2O	6 2	200	24	96.4	96.4
6	36.375	NH_4NO_3 Cu_2O	6 1	200	18	96.6	97.6
7	36.375	NH_4NO_3 Cu_2O	4 2	200	18	96.8	96.5
8	36.375	NH_4NO_3 Cu_2O	8 3	200	18	98.2	96.5
9	42.5	Control	..	200	20	94.6	91.6
10	42.5	NH_4NO_3	8	200	24	96.5	89.6
11	42.5	Cu_2O	1	200	24	92.7	88.2
12	42.5	NH_4NO_3 Cu_2O	8 1	200	24	94.2	95.3
13	42.5	$(NH_4)_2SO_4$ Cu_2O	6 2	195	24	95.4	92.5
14	36.375	NH_4ClO_4 Cu_2O	4 3	200	18	98.0	95.6
15	36.375	NH_4Cl Cu_2O	4 1	200	18	95.6	94.6
16	36.375	$NH_4C_2H_3O_2$ Cu_2O	5.8 1	200	18	95.8	94.6

[a] Capacity of autoclave, 500 cc.; 28% aqueous ammonia, 315 grams.

EFFECT OF TYPE OF ORGANIC COMPOUND ON USE OF COPPER CATALYSTS

Ethylene dichloride can readily be converted to ethylenediamine by treatment with aqueous ammonia at 110° C. without employing a catalyst. It will be shown later that 2-chloroanthraquinone can also be converted readily to an amine of high purity at 180–200° C. without the introduction of metal catalysts. In the treatment of compounds containing a halogen substituent attached to a phenyl nucleus—viz., chlorobenzene, chlorophenylanthraquinones, and chlorobenzoylbenzoic acids—copper catalysts are practically indispensable. In a future publication it will be shown that the presence of copper compounds is advantageous also in the amination of dichloroanthraquinones.

In Table III the data show that the ammonolysis of 4′-chloro-2-phenylanthraquinone is not practicable unless a copper compound is used. The results also reveal that in the presence of ammonium nitrate and potassium chlorate the yields and purity of the amine are about the same when copper powder is substituted for cuprous oxide. It is important to observe that the combination of oxidant and copper catalyst is directly productive of an excellent product with high yields.

POTASSIUM CHLORATE WITH COPPER COMPOUNDS

The inclusion of an oxyhalogen compound along with a copper compound appreciably improves the results in the amination of 2-chloroanthraquinone. The controls at 195–200° C. without catalysts of any character appear to be about as good as those containing a copper compound alone. At lower temperatures (Table I), however, experiments containing a copper compound showed an improvement over controls. In Table IV are presented data relating to the ammonolysis of 2-chloroanthraquinone which show the effect of using potassium chlorate along with a copper catalyst.

Ammonium Salts and Copper Compounds

When ammonium nitrate was used in conjunction with cuprous oxide in the ammonolysis of 2-chloroanthraquinone, the results were always better than when either one alone was used. In fact, the addition of any ammonium salt to cuprous oxide by exerting a common ion effect contributes to an improvement in both the yield and purity of the amino compound. The data in Table V show that under optimum conditions a satisfactory product can be obtained.

Literature Cited

(1) Arnold, U. S. Patent 1,799,722 (1931).
(2) Groggins and Newton, Ind. Eng. Chem., 21, 369 (1929).
(3) Groggins, Stirton, and Newton, *Ibid.*, 23, 893 (1931).
(4) Hale and Britton, U. S. Patent 1,607,824 (1926); reissue 17,280 (1929).
(5) Hotz, U. S. Patent 1,690,785 (1928).
(6) Imperial Chemical Industries, Ltd., French Patent 717,538 (1932).
(7) McMaster and Steiner, Ind. Eng. Chem., 22, 547 (1930).
(8) Reppe, U. S. Patent 1,762,742 (1930).
(9) Schweitzer, U. S. Patent 1,806,714 (1931).
(10) Tobler, U. S. Patent 1,699,894 (1927).

Received October 10, 1932. Part I is Contribution No. 214, and Part II No. 215 from the Color and Farm Waste Division, Bureau of Chemistry and Soils. Other parts will be printed in February and March.

Pipe-Line Protection

Stanley Gill, Rusk Building, Houston, Texas

No attempt is made to present detailed data upon the application and performance of the several classes of coatings which are discussed. The general status of the art of pipe-line protection is described.

In general, it may be stated that, although there are available coating systems which make possible economical protection of pipe lines, there remains a large field for development of improved methods for preventing the great losses which corrosion forces upon the pipe-line industry.

DEVELOPMENT of improved coatings for the protection against corrosion of buried pipe lines is a problem of the utmost economic importance. Shepard (*9*) estimates that there are in the United States approximately 450,000 miles of buried pipe lines. At a conservative estimate these lines contain not less than 30,000,000 tons of steel, all of which is exposed to more or less severe corrosive attack. Approximately half of the total mileage is in trunk line systems for the transportation of oil and gas, the remainder being in distribution systems within cities, etc. The trunk line systems consist almost entirely of large-size steel pipe, oil lines being made up of 4- to 12-inch pipe and gas trunk lines of 8- to 24-inch pipe. The distribution systems are of smaller sizes, and considerable cast-iron pipe is used. Shepard (*9*) estimates that the annual loss by corrosion of these lines is $142,500,000. His estimate compares favorably with that prepared by Speller in 1927 (*10*). It is probable that these figures are considerably higher than the actual loss of metal caused by the corrosion, but they are certainly lower than the actual total expense entailed by corrosion of pipe lines.

The tremendous economic loss arising from corrosion of buried pipe illustrates the importance of the problem which confronts manufacturers of protective coatings for pipe lines. Although there are at present coating systems which can be depended upon to reduce greatly corrosion of buried lines, all are subject to certain objectionable features. The problem is by no means solved, and an extremely promising field is presented to the coating manufacturer who can develop a protective method which will economically reduce soil-corrosion losses.

Requirements for Satisfactory Pipe-Line Coatings

Extensive investigation of the performance of pipe-line coatings has served to develop but one general principle covering their performance. This has been expressed as follows (*4*):

> Impermeability to moisture—which should not be confused with waterproofness—is the most important single requirement for a coating which will protect metal against soil corrosion. A coating which positively prevents access of moisture to the metal's surface will preclude the possibility of corrosion. If moisture is in contact with the metal surface, corrosion may or may not proceed, depending upon other conditions.

In general, any coating which meets this condition, and which continues to meet it after prolonged exposure to soil action will satisfactorily protect buried metal. It is not impossible that a satisfactory coating could be devised which would not satisfy this requirement, but it is certain that this has not been done up to the present time.

Continued impermeability of pipe-line coatings depends upon the following factors: (1) resistance to deterioration from chemical or bacterial action, (2) freedom from capillary pores, and (3) resistance to mechanical distortion. Of these, the third is perhaps the most important cause of failure in existing protective coatings. The principle of mechanical distortion of pipe-line coatings was developed by Scott (*7*) and was termed by him "soil-stress action." Scott's work, which has shown the prevalence and importance of soil stress in the destruction of pipe-line coatings, has been of the utmost importance in establishing present methods of pipe-line protection, which almost universally incorporate means for protecting the coating material against mechanical distortion.

Fully as important as the ability of a coating to afford continued protection are the limitations imposed by economic considerations. Much work has been done to determine the extent to which the use of coatings is economically justified. Very little of this has been published, although the general principles were enunciated by Weidner (*12*) in 1926. A later discussion of the economics of pipe-line protection has been contributed by Truett (*11*) and by Weidner (*13*). Obviously, the justification for the use of coatings depends upon the severity of the corrosive conditions and upon the cost and effectiveness of the coating system. Extended use of coatings is justified by increasingly severe corrosive conditions, by increased effectiveness of coatings, by increased cost of lines, by increased protection efficiency of coatings, and by decreased cost of coating systems. These factors must be carefully considered in the development of a pipe-line coating, as must also the adaptability of the coating to application under the rather difficult conditions which prevail during the construction of a pipe line.

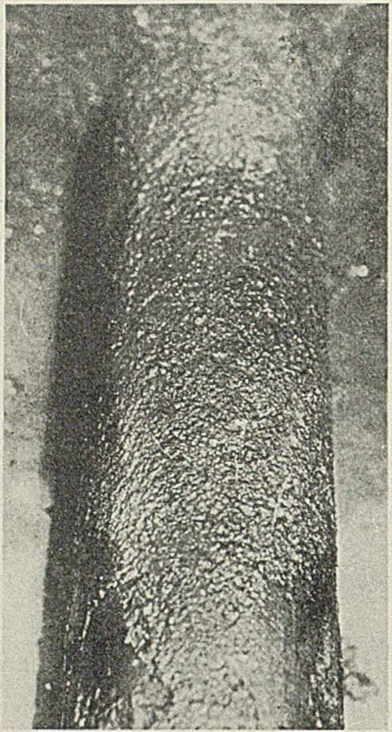


Figure 1. Typical Failure of Bituminous Pipe-Line Coating Due to Soil-Stress Action

Within the scope of this paper it is not possible to consider in detail all of the types of pipe-line coatings which have been used, or which are now under consideration. A great amount of work is being done on the development of pipe-line coatings, and rapid advances are being made. A comprehensive view of the present status of this work is given by progress reports on the work of Scott (*8*) and Ewing (*1*). The following description covers briefly the various classes of coatings, and is intended to serve as a rapid survey of the field, rather than as a detailed description of the advantages and disadvantages of the various coating materials.

Oil Paints

Among the earliest attempts to protect buried pipe lines was the use of the usual types of metal protective paint, particularly red lead. Although occasional instances of satisfactory performance of such paints have been reported, they are, generally speaking, inapplicable for the purposes. Apparently their failure is caused by saponification of the oil film, although the permeability of the film may also contribute to their failure. The writer has observed cases of severe pitting of pipe under apparently unbroken films of red lead paint.

It has been suggested by Speller and others that coatings of excellent protective value could be obtained by baking oil-paint films. This proposal is based upon the numerous observations of cases in which markings made in the mill with white lead and red lead paints while the pipe was still hot have remained intact for many years of underground exposure. It is possible that the work being done on this line will produce worthwhile results, although as yet there are no conclusive data upon the performance of such coatings.

It is also probable that the performance of certain classes of bituminous coating materials can be improved by using, in conjunction with them, corrosion-inhibitive oil-paint primers. Tests of combined coatings of this type are now in progress.

Bituminous "Cut-Backs"

Of coatings which are applied cold, solutions of bitumens (both coal tar and asphalt) have been most widely employed. Such coatings possess the advantages of cheapness and ease of application, and these considerations have caused them to be used on many thousands of miles of pipe lines.

Generally speaking, coatings of this class are of little or no value for the protection of pipe which is exposed to destructive soil corrosion. This statement applies with almost equal truth to the comparatively few cut-back coatings which have been made with some degree of technical supervision, and to the far greater number of coatings which have been made of the cheapest material available, and sold merely with an eye to profit.

The failure of bituminous cut-back coatings is caused almost entirely by their great permeability to soil moisture. By proper selection of bitumen, they may be made to possess a satisfactory chemical stability; but all are more or less permeable to moisture, and even those which possess a relatively high initial impermeability are rapidly destroyed by soil-stress action.

The present tendency in pipe-line protection is to eliminate entirely the use of bituminous cut-backs. This practice is warranted by their proven lack of protective value; but there remain many lines on which, because of their temporary nature or a mild corrosive environment, cut-backs can be economically used. Cut-backs are widely employed as primers under bitumens which are applied in a molten condition.

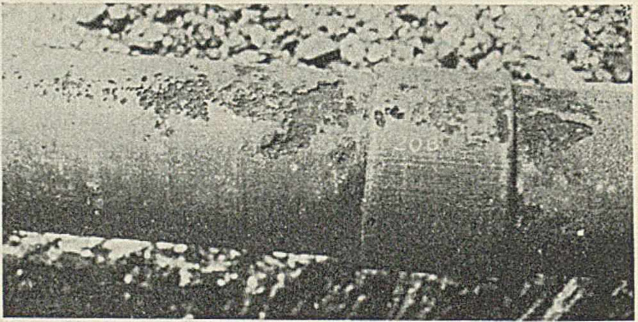


Figure 2. Typical Corrosion of Steel Pipe Line

Asphalt Emulsions

Within recent years asphalt emulsions have been applied to pipe lines in an attempt to prevent corrosion. Some of these emulsions carry chromate inhibitors. The asphalt emulsion coatings have not been at all successful on buried pipe lines. They are exceedingly permeable, and this permits corrosion to proceed, even where they are thoroughly protected against soil-stress action, to which they are particularly susceptible. Recently applied combinations involving asphalt emulsions sheathed with Portland cement mortar may be expected to give good protection; but it is difficult to say how much of the protection is to be attributed to the asphalt, and how much would be afforded by the cement mortar alone.

On the whole, asphalt emulsions offer but little promise as pipe-line protective coatings.

Greases

Special greases have been developed and extensively employed for the protection of buried pipe lines. These greases are based upon crude petrolatum stock, in combination with soaps or thinners to give the desired consistency, and with or without added inhibitive materials. The greases possess, in comparison with bituminous materials, the advantage of a far greater inherent impermeability; hence, a thinner film is required for protection. This advantage is more than overbalanced by the fact that the greases possess no mechanical strength, and are consequently punctured under the slightest soil pressure. In addition, they are absorbed by soils, in many of which an unwrapped grease coating will disappear completely within a few months. In combination with suitable wrapping materials, grease coatings will give good protection; but it is essential that the wrapping material shall itself be quite impervious, as otherwise the grease may be absorbed by the soil.

There is one exception to the generally unsatisfactory performance of unwrapped grease coatings. In many instances, coatings of this type have given good protection on lines laid in swamps where the pipe was continually wet, and where there was little or no soil pressure.

Lacquers and Synthetic Resins

There have been no extensive field tests of pipe-line coatings of the lacquer type, or of coatings based upon any of the recently developed synthetic resins. Isolated tests of individual coatings of this class have been made; results have been quite unsatisfactory, but this should not be taken as a condemnation of the possibility of developing, by studies along this line, a class of pipe-line coatings which will be less expensive for a comparable degree of protection than those which are now in use.

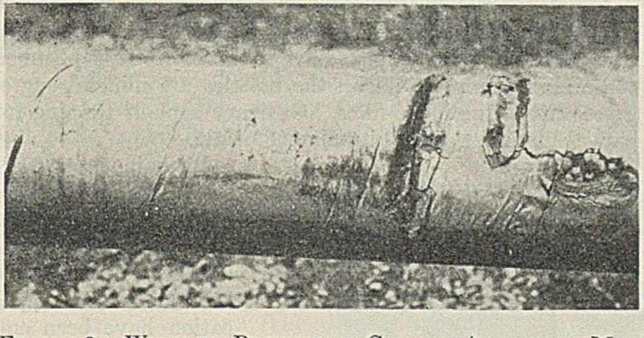


Figure 3. Wrapped Bituminous Coating Applied at Mill and Shipped in Coated Condition

Shows great defect in mill-wrapped coatings, which is mechanical damage in handling.

The main advantage of lacquer or resin type coatings as compared to bituminous materials lies in the fact that the films formed would not be subject to soil-stress action; that is, they would not flow as a result of pressure or contraction and expansion of the soil. It is entirely possible to develop synthetic resin films which possess a high degree of impermeability. The writer has tested a great number of coatings of this class which were designed for the protection of tanks against corrosion by hydrogen sulfide, and many of those examined were extremely impervious. The main difficulty probably lies in the development of a combination which will not be saponified by soil waters; this difficulty should not be insuperable.

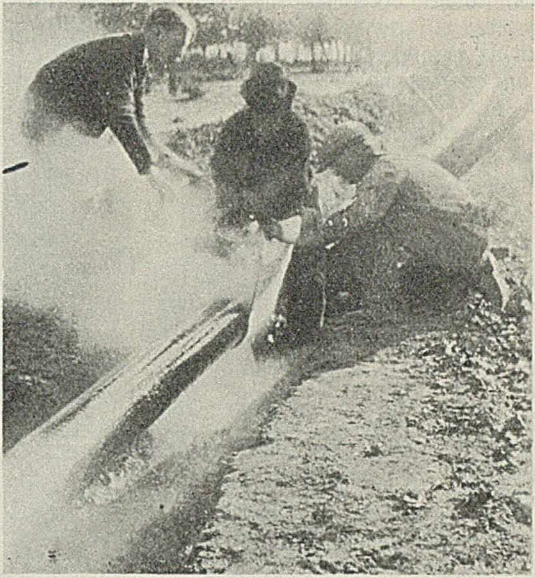


Figure 4. Field Application of Molten Coal-Tar Pitch Coating

Many such coatings give off highly objectionable fumes.

This line of investigation appears to offer great possibilities for the development of inexpensive coatings which could be easily applied under field conditions, and which would afford appreciable protection without the use of wrapping materials.

Molten Bitumens

The most effective coating systems which are at present available are those which involve bitumens applied in a molten condition. The earliest coatings of this class were asphalts which were applied to the pipe without wrapping. Asphalts are still extensively employed, and give good protection when used in conjunction with properly selected and applied wrappings. Essentially, modern coatings of this class comprise a priming coat of cut-back asphalt, one or two thick coats of asphalt applied in the molten condition, and a wrapping of asphalt-saturated felt, over which is usually applied another coating of molten bitumen. The wrapping may be applied longitudinally, in which case a strip of felt having a width approximately equal to the circumference of the pipe, and from 6 to 20 feet in length, is applied over the bitumen while it is still molten, or the felt may be wrapped spirally. Spiral wrapping results in better coating jobs, as the felt can be pulled more tightly into the bitumen, eliminating the bagging which is experienced with longitudinal wrapping. Within recent years there have been developed machines by which spiral wrappings are applied either at the pipe mill, at centrally located points, or in the field while the line is under construction. These machines do excellent work, and the wrapped coatings prepared by their use are far superior to most of the work which was previously done by hand.

In general, by properly selecting asphalt and wrapper and by exercising proper care in application, coatings of good protective value can be obtained. Certain petroleum asphalts are entirely unsuitable for pipe-line protection, being subject to rapid deterioration; others have been found to be exceedingly stable when exposed to soil action. Asphalts should never be used without the protection of a wrapper.

At the present time by far the most widely used class of pipe-line protective coatings are the so-called coal-tar enamels. These consist of combinations of coal-tar pitch with mineral fillers, such as silica, volcanic ash, or flake mica. In some cases natural asphalts have been blended with the coal-tar pitch and filler. As a class the enamels have melting points (ring and ball) ranging from 160° to 210° F., with a melting point of approximately 190° F., representing an average of present-day enamels of high melting point. The enamels are applied to pipe which has been previously primed with a suitable cut-back bituminous coating at a temperature of 350° to 500° F. When the enamels are properly compounded and are applied with adequate care and at proper temperature, the coatings obtained range in thickness from $^1/_{32}$ to $^1/_{16}$ inch and possess a high resistance to penetration by soil moisture.

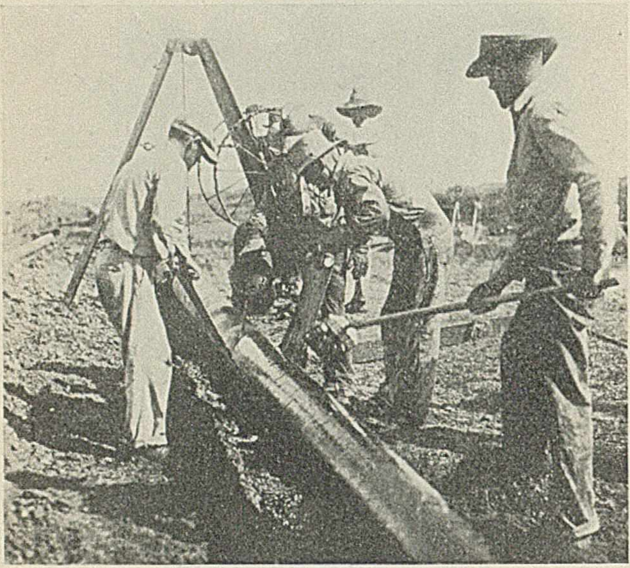


FIGURE 5. FIELD APPLICATION OF MOLTEN BITUMINOUS COATING

Coating is poured on line distributed by canvas sling; brush is used to touch up spots not coated by sling

Coal-tar enamel coatings will afford protection, under some conditions without the use of wrappers. Scott (*7*) has shown, however, that they are subject to severe mechanical distortion in many soils. His work has resulted in the present tendency to use enamels of high melting point, low susceptibility, and low penetration. It has also resulted in the present practice of protecting enamel coatings against soil stress by the use of suitable wrappers wherever maximum protection is required.

The wrapped enamel coatings, which probably possess greater protective value than any currently available coatings of comparable cost, fall into two classes, depending upon whether the wrapper is applied while the bitumen is still molten (giving a "bonded wrap"), or whether the wrapping is applied loosely over a chilled enamel layer (giving an "unbounded wrap"). The relative merits of these two classes of wrapped enamel coatings are still in dispute; but both, when the work is properly performed, will give coatings of high protective value.

Under especially severe conditions, molten bitumens, particularly asphalt, have been applied in thicknesses of 1 to 2 inches. This application is performed by first priming the pipe, and then inclosing it in a wooden box or metal shell, made either from pipe of a larger size or from light-gage sheet iron. This is spaced from the pipe to give the desired thickness of coating, and is poured full of molten bitumen. Such a coating is too expensive for ordinary use, but may be economically justified by exceptionally severe corrosive conditions, or by a need for insulation against stray currents at relatively high potentials.

PIPE-LINE WRAPPERS

A great variety of materials has been used or suggested for wrappings over bituminous pipe-line coatings (*2*). The most widely used, and at present the most satisfactory, wrapping materials are bitumen-saturated felts, similar in general character to those which are used for roofing. These felts are classed as rag or asbestos felts, and are saturated with coal-tar pitch, asphalt, or petrolatum, depending upon the type of coating with which they are to be used. Generally speaking, the asbestos felts are most satisfactory for the purpose, since rag felts have been found to deteriorate when exposed to certain soils.

Many other types of wrapping materials are at present under investigation. Of particular interest is the use of metal foil, about 0.002 inch thick, for the purpose; copper foil seems to offer great promise as a pipe-line wrapper. Of the other new materials which are now being tested, reënforced sheets of Cellophane and papers impregnated with synthetic gums also afford some promise.

BITUMINOUS MASTICS

A certain amount of research work is being done upon the protection of buried pipe lines by the use of bituminous mastics. The pipe-line enamels have been described as bitumen containing a mineral filler; the mastics are mineral aggregates with bituminous filler. Ordinary asphalt topping for pavements is a typical bituminous mastic.

Bituminous mastics for the protection of pipe lines are applied mechanically to a thickness of $^3/_8$ inch or more. Two methods of application have been employed. In the first, the mastic is extruded around the pipe; in the second, it is applied to a band of fabric which is wrapped spirally around the pipe on a wrapping machine, forcing the mastic tightly against the pipe surface.

The tests which have been carried out show that the mastic coating thus applied affords excellent protection

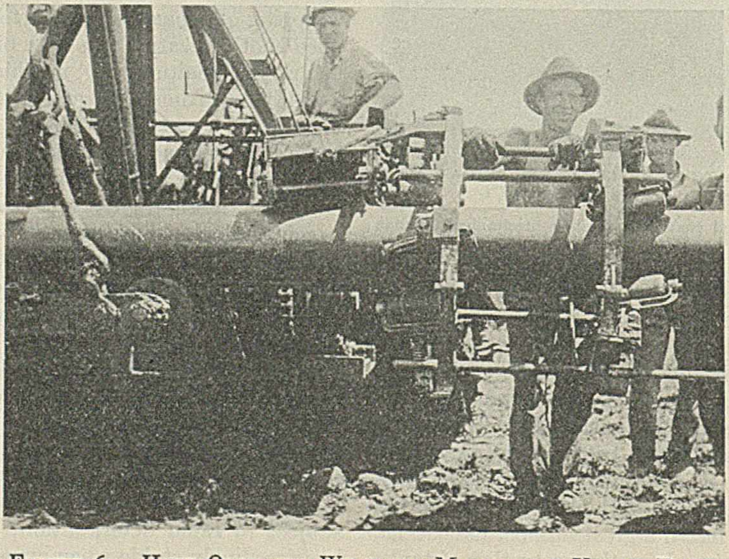


FIGURE 6. HAND-OPERATED WRAPPING MACHINE IN USE IN FIELD, APPLYING SPIRAL WRAPPING OF ASBESTOS FELT

against soil corrosion, and is not appreciably affected by soil-stress action. However, the necessity for mechanical application at the mill or centrally located yard, and the difficulty of protecting the joints between coated sections in the field will probably limit the application of mastic coatings to protection of short stretches of line which are exposed to exceptionally severe corrosive conditions.

Portland Cement Coatings

Combinations involving Portland cement have been used for a number of years to protect pipe lines against soil corrosion. Both concrete and mortar have been used for the purpose; generally speaking, mortar has been found to afford better protection, since the concrete has been more or less porous. Experience has shown that a properly applied cement mortar coating will afford lasting protection against soil corrosion under almost any conditions. The objections to cement coatings are the relatively high cost of application, and the fact that pipe so coated cannot be economically recovered for re-use if the pipe line is abandoned.

Early applications of concrete and mortar for pipe-line protection were made by the use of boxes, metal molds, or troweling, the mortar being applied to a thickness of one inch or more, and usually reënforced by the use of chicken wire or a similar material. Such coatings are still affording excellent protection after many years of service. The expense of such application is great, being in some cases as high as $10,000 for a mile of 10- or 12-inch pipe. Mortar has also been applied to pipe lines by the use of the cement gun. A coating applied in this manner over suitable reënforcement, and $^{3}/_{8}$ to $^{5}/_{8}$ inch in thickness, is a highly effective protective coating.

Engineers of the Indiana Pipe Line Company have recently developed a practical field method for the application of cement mortar coating, using movable metal molds (*3*). A particularly important feature of this method is that it has been worked out with a view to the conditions encountered in pipe-line operation. The detailed practical knowledge involved in this development has resulted in a method which is exceedingly inexpensive, being comparable in cost to many of the commonly used bituminous coatings.

Recent work has also been done by the Portland Cement Research Association upon the application of concrete to pipe lines by the use of movable metal forms and vibrators (*5*). The coatings produced are about one inch thick and are exceptionally dense and impervious. The method affords great promise, although it has not as yet been extensively applied in the field.

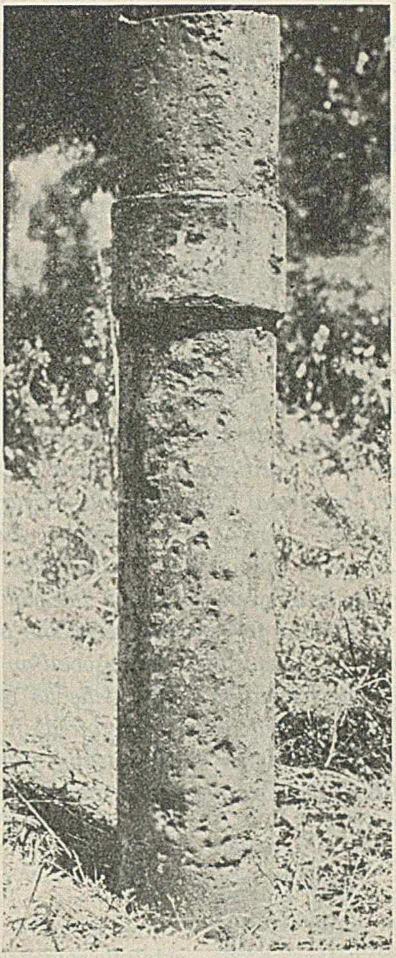


Figure 7. Section of Steel-Lined Pipe Cut Out of Service after Two Years

An interesting development in the application of Portland cement for pipe-line protection has been reported from Italy (*6*). This involves a wrapping fabric made of a mixture of fiber asbestos and Portland cement. The wrapping material is built up in thin layers to the proper thickness, and is wrapped spirally on the pipe to a thickness of 2 to 4 mm. (0.08 to 0.16 inch). A bituminous coating is applied over the cement wrapper. This method has never been applied or tested in the United States but seems to offer exceptional promise.

Vitreous Enamel

Improvements in the quality of vitreous enamels have led to their application for protection of pipe lines. Pipe coated with vitreous enamel has been marketed during the past few years in Germany, and a large American manufacturer of pipe is now equipped to supply a similar coated pipe. Ingenious methods have been developed for protecting the uncoated joints, and for repairing breaks in coating which occur during laying.

Since there have been no lines laid with this pipe, and since no data on its performance in actual lines are available, no conclusion as to its merit can be drawn. It involves special handling during laying, and it is possible that pinholes or invisible cracks developed during laying may deprive it of protective efficiency. It is possible, however, that vitreous enamel coatings will afford excellent protection, and that they will find wide application in pipe-line practice.

Literature Cited

(1) Ewing, *Oil Gas J.*, 28, 47 (1930).
(2) Gill, *Oil Weekly*, 60, 40 (May 8, 1931).
(3) Hough, *Oil Gas J.*, 29, T-78 (June 4, 1931).
(4) Langford (quoting Gill), Am. Petroleum Inst., *Bull.* 10, No. 2, Sect. I, 93–9 (1929).
(5) Portland Cement Assoc., *Tech. Data Sheet*, 28 (1930).
(6) Rocca, *Korrosion u. Metallschutz*, 6, 207 (1930).
(7) Scott, Am. Petroleum Inst., *Bull.* 10, No. 2, Sect. I, 78–93. (1929); *Development Production Eng. Bull.* 204, 136–45 (1930).
(8) Scott, Am. Petroleum Inst., *Bull.* 208, 55–107 (1931).
(9) Shepard, *Gas Age-Record*, 68, 333 (1931).
(10) Speller, Am. Petroleum Inst., *Bull.* 8, No. 6 (1927).
(11) Truett, *Oil Gas J.*, 29, T-45 (June 4, 1931).
(12) Weidner, Am. Petroleum Inst., *Bull.* 8, No. 6, 352–6 (1927).
(13) Weidner, Am. Petroleum Inst., *Development Production Eng. Bull.* 204, 132–5 (1930).

Received April 7, 1932. Presented before the Division of Paint and Varnish Chemistry at the 83rd Meeting of the American Chemical Society New Orleans, La., March 28 to April 1, 1932.

* * *

Equilibrium Dehydrogenation of Ethane, Propane, and the Butanes

F. E. Frey and W. F. Huppke, Phillips Petroleum Company, Bartlesville, Okla.

Ethane, propane, n-butane, and isobutane are dehydrogenated to the corresponding olefins and hydrogen at 350° to 500° C. and 760 mm. pressure by means of a catalyst prepared from air-dried chromic oxide gel. Equilibrium dissociation is obtained with little interference from side reactions, and equilibrium constants are determined for the several hydrogenation-dehydrogenation reactions. Extent of dissociation increases with increase in the number of alkyl substituents attached to the ethylene group in the olefin produced. n-Butane forms all three of the possible n-butenes. The equilibrium dissociation is the same for the formation of 1-butene as for propylene. Both 2-butenes are produced in higher concentration, the lower boiling (trans) isomer being a little the more abundant and hence more stable.

THE formation of paraffins from the corresponding olefins by combination with hydrogen has been shown to take place readily at moderate temperature in the presence of suitable catalysts, such as cobalt, nickel, copper, iron, silver, platinum, and palladium (*13*).

The dehydrogenation of paraffins to olefins and hydrogen, however, is thermodynamically possible only at somewhat elevated temperatures. At such temperatures copper loses activity (*11*), and nickel, platinum, and palladium bring about a complex decomposition (*3*). Dehydrogenation has been reported, however.

Tausz and Putnoky (*16*) passed the vapors of pentane, hexane, heptane, and octane over palladium at 300° C. and obtained hydrogen and a small amount of unsaturated hydrocarbons. The I. G. Farbenindustrie Akt.-Ges. (*7*) reports that amylene was the chief product formed when pentane was passed over activated charcoal at 450° to 500° C.

In the course of a study of catalytic reactions of hydrocarbons, a catalyst was prepared from chromic oxide gel which brought about the dehydrogenation of simple paraffins into the corresponding olefins at 350° to 500° C. Side reactions were not marked under proper conditions, and hydrogenation as well as dehydrogenation took place without serious complications. In the present study this catalyst was used to bring about equilibrium in mixtures of several paraffins—namely, ethane, propane, *n*-butane, and isobutane, with their dissociation products, and thus to determine by direct measurement the equilibrium constant for every possible reaction of the type:

$$C_nH_{2n+2} \rightleftarrows C_nH_{2n} + H_2$$

The ethane-ethylene equilibrium has been determined directly by Pease (*12*). Ethane decomposes into ethylene and hydrogen, and ethylene and hydrogen unite to form ethane at 600° to 700° C. in the absence of a catalyst and without excessive side reaction; satisfactory equilibrium values are obtained by approaching equilibrium from both sides at these temperatures. The higher paraffins, however, decompose under such conditions through fracture of carbon-carbon bonds as well as dehydrogenation. Consequently, this method is not applicable to them and the use of the catalyst is required. In the experiments to be described, propane was found to be more highly dissociated into olefin and hydrogen at equilibrium than ethane, and isobutane was still more highly dissociated; the dissociation amounted to 1.2, 4.5, and 9.2 per cent, respectively, for ethane, propane, and isobutane at 400° C. and 760 mm. pressure. *n*-Butane exhibited a high extent of dissociation (8.5 per cent under the same conditions) by reason of the fact that equilibrium concentrations of all three of the normal butenes—namely, 1-butene and the *cis* and *trans* isomers of 2-butene—were formed independently. A study of the dehydrogenation of other hydrocarbons is in progress.

It is also possible to determine equilibrium constants or free energy change for the dissociation of paraffins by calculation from thermal data (*4, 10, 17*), but the possibility of appreciable errors arising from small errors in heats of combustion has been recognized, and the direct determination is accordingly desirable particularly for comparing the stabilities of isomeric olefins.

Experimental Procedure

Apparatus and Method. The apparatus used for the catalytic conversion is shown in Figure 1.

The gas to be treated passed through drying tube *A* containing magnesium perchlorate trihydrate, through flowmeter *B* and was delivered at a pressure of 760 mm. indicated by manometer *C* into catalyst tube *E* of Pyrex glass, 7 mm. in inside diameter and containing a 5-cc. portion of granular catalyst. In order to obtain an even reaction temperature, a heavy steel sheath, *F*, was located inside the furnace, *D*, and surrounding the catalyst tube. Thermocouple *G*, at the inner surface of *F*, was used to measure the temperature, and in some instances a thermocouple imbedded in the catalyst near the exit was used to insure that the reaction temperature was correctly shown by *G*. The gas leaving the catalyst tube was discharged through bubbler *H*, and a sample for Orsat analysis was drawn into *I* when the desired conditions had been established. Large samples for fractionation analysis were taken into a large evacuated bottle, or condensed at liquid nitrogen temperature when the determination of hydrogen and methane were unnecessary.

Materials. The ethane was prepared from a commercial product containing a little ethylene. The ethylene was removed by passing repeatedly through fuming sulfuric acid and finally sodium hydroxide solution, after which the ethane was condensed and purified by fractional distillation. Propane, *n*-butane, and isobutane were prepared from natural gas condensate by careful fractionation. None of the hydrocarbons contained more than one per cent of homologs or isomers except the isobutane, which contained 1.5 per cent *n*-butane. No more than traces of other impurities were present. The propylene was a pure commercial product. 1-Butene was prepared by the interaction of allyl bromide and methylmagnesium iodide, and purified by fractional distillation.

Preparation of Catalyst. Eight hundred grams of Baker's c. p. chromic nitrate hydrate were dissolved in 8 liters of distilled water, and the solution was clarified by filtration. A solution of 400 grams of ammonium acetate in 16 liters of distilled water was then added. To the mixture at a temperature of 50–60° C. were added rapidly with stirring 8 liters of distilled water containing 650 cc. of concentrated ammonium hydroxide (28 per cent ammonia). After 2 hours the gelatinous precipitate was filtered off on a Büchner funnel, washed three times by stirring into 30 liters of hot distilled water and filtering, and finally dried in an air bath at 50° C. The dried gel was black and vitreous in texture and appearance. After crushing and screening to a size of 10–40 mesh to the inch, the gel was further dried *in vacuo* for 8 hours while the temperature was raised gradually to 250° C., after which it was ready for use. A 5-cc. portion was then placed in the catalyst tube and electrolytic hydrogen, purified by passing through copper gauze at 400° C. and magnesium perchlorate trihydrate, was passed through while the temperature was gradually raised to 400° C. over a period of 5 hours. Pure propane under atmospheric pressure was then passed over the gel at 400° C. at a rate of 10 liters per hour for the 5-cc. portion of granular catalyst. Dehydrogenation activity gradually developed and full activity was reached in several hours with the formation of nearly equilibrium concentrations of about 4 per cent each of hydrogen and propylene. The black vitreous appearance of the catalyst remained unchanged throughout.

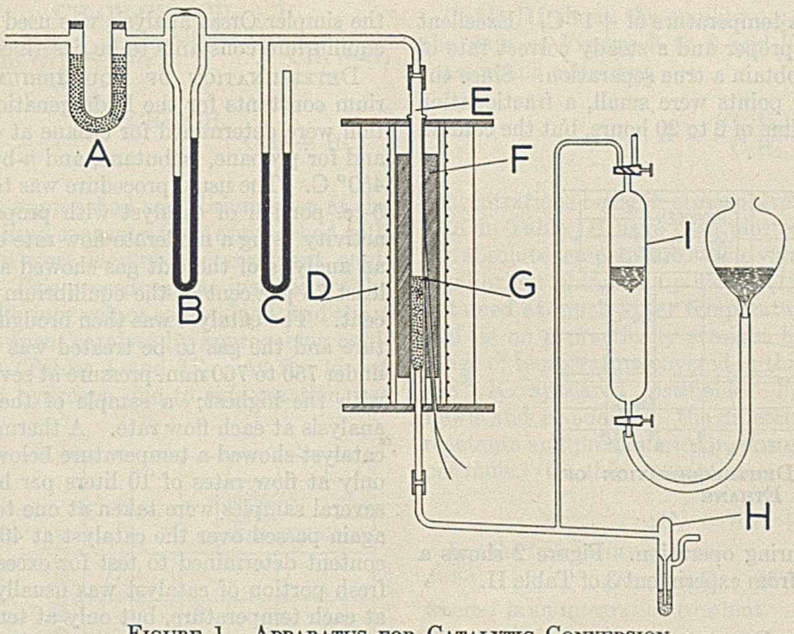


FIGURE 1. APPARATUS FOR CATALYTIC CONVERSION

ANALYTICAL METHODS

The determination of olefins and hydrogen was carried out in an Orsat apparatus (*1*) connected by glass-to-glass seals to avoid the solvent effect of rubber. A mercury-filled gas pipet was used for the determination of olefins by sulfuric acid absorption. Portions of acid (1 cc.) were used to minimize absorption of paraffins. Ethylene, propylene and *n*-butenes, and isobutylene were determined by absorption in fuming (10 per cent sulfur trioxide) 85 per cent and 65 per cent acid, respectively. Because of the marked tendency of the butane to dissolve in stopcock grease, a soap-glycerol lubricant was used in the analysis of samples high in butane.

In several cases the analysis of the products of reaction was carried out with the aid of fractional distillation, and in this way by-products were determined which could not be determined by the simpler Orsat method described. The result of fractionation analysis, however, showed that the Orsat method was adequate for the greater part of the work. In the fractionation method, the products of the catalytic reaction were fractionated in a column of the type described by Oberfell and Alden (*9*) and Podbielniak (*14*). All material boiling lower than the paraffin treated (and its corresponding olefins) consisted of hydrogen and by-products. This material was separated by the column and subsequently analyzed by the Shepherd-Porter method (*5, 15*) which is suitable for handling small quantities. The main paraffin-olefin fraction was then distilled overhead for separate examination. Little higher-boiling material was found.

ANALYSIS OF BUTENES BY FRACTIONAL DISTILLATION. Since the dehydrogenation of *n*-butane produced three isomeric *n*-butenes, special analytical means were necessary for determining each individually. After isolating the butane-butene fraction, the butenes were separated from butane in the following manner: They were converted into bromides by titrating the fraction with liquid bromine at −40° to −60° C. The addition was discontinued when a decided bromine coloration persisted after several minutes at −10° to −20° C. The butane was then distilled off without ebullition at −75° C., and, since the formation of the tetrabromide from butadiene dibromide takes place somewhat slowly, an excess of one per cent of bromine was added and the mixture kept at 0° C. for 15 hours to complete the addition of bromine to the butadiene. The excess bromine was then removed by aqueous sodium sulfite, after which the bromides were distilled at +40° to +60° C., and 0.5 mm. pressure. The distillation residue of semi-crystalline butadiene tetrabromide was estimated by weighing. Under these conditions, substitution reactions did not take place appreciably. The distillate containing only the dibromides was then converted back into butenes by treating with zinc dust in 85 per cent ethyl alcohol. The butenes were distilled from the alcohol through a calcium chloride tube into a fractionating column for separating the isomers. Yields of 95 to 100 per cent were obtained. By analyzing synthetic mixtures, it was shown that the composition of a mixture of the isomeric butenes was changed little by this sequence of operations.

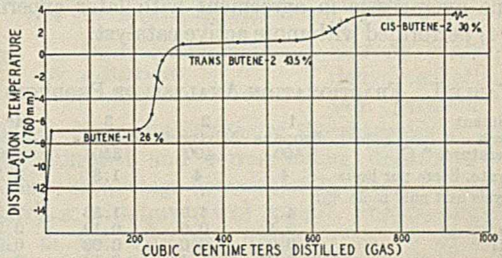


FIGURE 2. FRACTIONATION OF BUTENES FROM *n*-BUTANE

(Table II, experiment 3)

The determination of the individual *n*-butenes is somewhat difficult because of their similarity. The boiling point differences are small, but, since a fractionating column capable of giving an analytical separation was available, it was used for the purpose. The boiling points are as follows: 1-butene, −6.5° to −6.7° C. (748 mm.); *cis*-2-butene, +2.95° to +3.05° C. (746 mm.); *trans*-2-butene, +0.3° to +0.4° C. (744 mm.) (*2*). The column used was a modified form of the type referred to, with a 2.5-mm. inside diameter of the column proper, and it contained a helical wire filling. It operated at a constant reflux temperature of +1° C. Excellent insulation of the column proper and a steady correct rate of boiling were essential to obtain a true separation. Since the intervals between boiling points were small, a fractionation required the rather long time of 6 to 20 hours, but the column needed little attention during operation. Figure 2 shows a typical distillation curve, from experiment 3 of Table II.

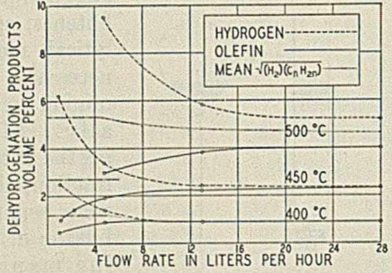


FIGURE 3. DEHYDROGENATION OF ETHANE

RESULTS OF DEHYDROGENATION

In order to determine the extent of side reactions and secondary reactions in addition to the predominating hydrogenation and dehydrogenation, propane, propane plus propylene plus hydrogen, and *n*-butane were passed over the catalyst at flow rates low enough to allow equilibrium to be established, and the products were analyzed by fractionation. The results are shown in Table I. A little falling off in activity took place during the collecting of enough of the product for fractionation analysis. Since equilibrium was established, the operating conditions were evidently favorable also for the hydrogenation of the olefins to paraffins. In experiments 1 and 2 the equilibrium for the reaction

$$C_3H_8 \rightleftarrows C_3H_6 + H_2$$

was approached from both sides. The composition of the exit gas is nearly the same for both experiments. The equilibrium constant calculated from the mean of the hydrogen-propylene averages is in agreement with later experiments (Figure 4) performed with more active catalyst.

TABLE I. FRACTIONATION ANALYSIS OF PRODUCTS

Experiment	1	2	3	4[a]
Inlet gas	Propane	Mixture[b]	Propane	*n*-Butane
Temperature, ° C.	400	400	350	400
Flow rate, liters per hour	4	4	1.8	3.5
Analysis exit gas, mole %:				
H_2	4.2	4.9	1.53	7.25
CH_4	0.5	0.6	0.19	0.38
C_2H_4	0.0	0.0	0.02	0.01
C_2H_6	2.0[c]	1.4[c]	0.14	0.24
C_3H_6	3.9	4.3	1.51	0.01
C_3H_8	89.4	88.8	96.61	0.24
C_4H_8	0.0	0.0	0.0	7.02
C_4H_{10}	0.0	0.0	0.0	84.85
Higher	0.0	0.0	0.0	0.0
Total	100.0	100.0	100.0	100.0

[a] Table II, experiment 3 shows composition of butenes produced in this experiment.
[b] The inlet gas contained hydrogen 9.7%, propylene 9.1%, propane 81.2%.
[c] These were early experiments and the ethane values are probably too high, since the Shepherd-Porter distillation was not used to purify fractions.

Experiments 3 and 4 show small proportions of methane, ethylene, and ethane produced by reactions involving the fracture of carbon-carbon bonds, in addition to the products of simple dehydrogenation. These by-products were evidently formed by catalytic action, since the temperatures were too low to cause appreciable homogeneous decomposition. Since they are virtually all paraffinic, hydrogenation equilibrium among these by-products having been established, the simpler Orsat analysis was used for the determination of equilibrium constants to be described.

DETERMINATION OF EQUILIBRIUM CONSTANTS. Equilibrium constants for the hydrogenation-dehydrogenation reaction were determined for ethane at 400°, 450°, and 500° C., and for propane, isobutane, and *n*-butane at 350°, 400°, and 450° C. The usual procedure was to treat at 400° C. a fresh 5-cc. portion of catalyst with propane to develop catalytic activity using a moderate flow rate of 10 liters per hour until an analysis of the exit gas showed a propylene content of at least 75 per cent of the equilibrium concentration of 4.5 per cent. The catalyst was then brought to the desired temperature and the gas to be treated was passed over the catalyst under 750 to 760 mm. pressure at several flow rates, beginning with the highest; a sample of the exit gas was taken for analysis at each flow rate. A thermocouple imbedded in the catalyst showed a temperature below that of the tube sheath only at flow rates of 10 liters per hour or more. After the several samples were taken at one temperature, propane was again passed over the catalyst at 400° C. and the propylene content determined to test for excessive loss in activity. A fresh portion of catalyst was usually taken for each paraffin at each temperature, but only at temperatures of 450° C. or higher did a marked loss in activity often take place in less than 4 hours' running time. A high activity was maintained for much longer periods under the best conditions.

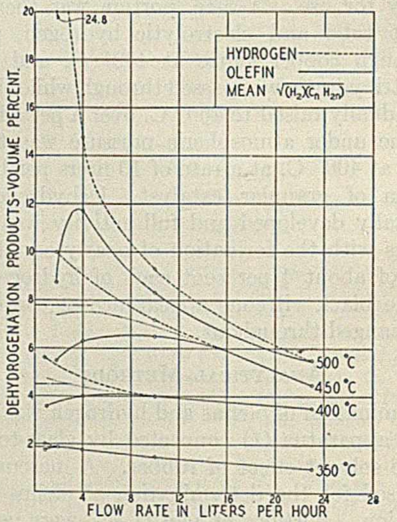
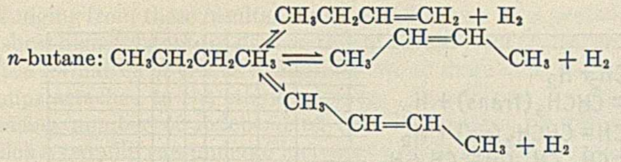


FIGURE 4. DEHYDROGENATION OF PROPANE

The samples were analyzed in the Orsat apparatus. Olefins were determined by sulfuric acid absorption, hydrogen was determined by copper oxide combustion, and the remainder was assumed to be the paraffin treated. These values were used to calculate equilibrium constants. At 450° and 500° C. this procedure involves appreciable errors, and since, moreover, the catalyst lost activity at high temperatures, the data obtained above 400° C. were given the least weight.

Figures 3 to 6 show the composition of the off-gas from the dehydrogenation of ethane, propane, isobutane, and *n*-butane at the several temperatures and flow rates; Table II shows the analyses for the individual butenes produced from *n*-butane in separate experiments in which equilibrium was not quite attained. Following Dillon, Young, and Lucas (*2*), the lower-boiling 2-butene has been designated the *trans* isomer. The reactions involved are as follows:

For ethane: $CH_3CH_3 \rightleftharpoons CH_2{=}CH_2 + H_2$
propane: $CH_3CH_2CH_3 \rightleftharpoons CH_3CH{=}CH_2 + H_2$
isobutane: $(CH_3)_2CHCH_3 \rightleftharpoons (CH_3)_2C{=}CH_2 + H_2$



Since dehydrogenation approached equilibrium even at the higher flow rates, the limiting concentrations approached with increase in contact time were assumed to represent equilibrium concentrations. This procedure was justified by the agreement between equilibrium values so obtained, and those obtained with somewhat spent catalyst by approaching equilibrium from both sides (Tables I and II). At the lowest flow rates an increase in hydrogen due to side reaction was associated with a corresponding decrease in olefin of the expected magnitude. A small part of the carbon is not accounted for in the gas analysis. This is due to the taking up of carbon by the catalyst, and to the formation of small amounts of polymer. Side reactions were most marked in the case of isobutane, the formation of methane leading to a deficiency in molecular hydrogen. The error in equilibrium measurements due to these effects is not great when the hydrogenation and dehydrogenation are rapid. At the highest temperatures and lowest flow rates a serious loss in catalyst activity resulted, and the data obtained under such conditions have been ignored.

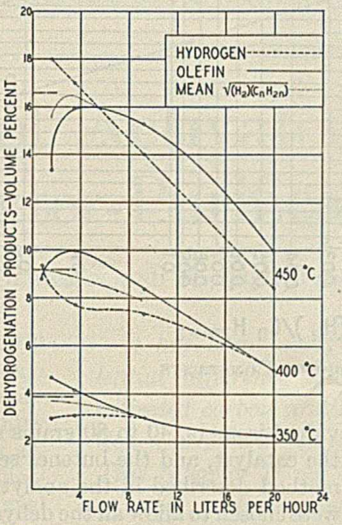


Figure 5. Dehydrogenation of Isobutane

Table II. Dehydrogenation of n-Butane

Experiment	1	2[a]	3	4	5
Temperature, ° C.	350	350	400	450	500
Flow rate, liters per hour	2.5	3.5	3.5	3.5	3.5
Analysis exit gas, mole %:					
H_2	3.8	3.7	7.2	14.0	...
C_4H_8	3.6	4.2	7.0	10.7	14.1
Composition of butene fraction:					
$CH_3CH_2CH:CH_2$	24	25	26	33	25
trans-$CH_3CH:CHCH_3$	48	45.5	43.5	39	74
cis-$CH_3CH:CHCH_3$	28	29	30	28	
$CH_2:CHCH:CH_2$	...	0.5	0.5	...	1
Total	100	100.0	100.0	100	100

[a] The inlet gas contained hydrogen 7.2%, 1-butene 7.7%, n-butane 85.1%.

Table III shows the equilibrium constants calculated from the data of Figures 3 to 6 and Table II according to the mass action equation:

$$K = \frac{(C_nH_{2n})(H_2)}{C_nH_{2n+2}}$$

concentrations being in atmospheres. In Figure 7, the values of K in Table III have been plotted against the reciprocal of the absolute temperature. The values for the ethane-ethylene equilibrium obtained by Pease (*12*) and the present values obtained at much lower temperatures are in good agreement and lie on a practically straight line. Because of the wide range of temperature covered in this case, an extrapolation to 298° K. appeared justifiable. Following the notation of Lewis and Randall (*8*), the difference in specific heat between reactants and products, ΔC_P, was estimated to be 4.0 calories per mole. On this assumption,

$$\Delta H_T = \Delta H_0 + 4.0T$$

For the free energy change,

$$\Delta F_T = \Delta H_0 - 4T \ln T + IT$$

where I is an integration constant.

From values of ΔF at two temperatures ($K_{723} = 0.00076$, $\Delta F = 10{,}326$; $K_{923} = 0.082$, $\Delta F = 4591$), ΔH_0 and I were evaluated ($\Delta H_0 = 27{,}798$; $I = 2.17$), and ΔF and ΔH at 298° K. calculated ($\Delta F_{298} = 21{,}653$; $\Delta H_{298} = 28{,}990$). Substituting in the fundamental equation:

$$\Delta F = \Delta H - T\Delta S$$

a value of 24.6 entropy units was found for ΔS_{298}. From the heat capacity data of Parks and Huffman (*10*) the entropy change for the dehydrogenation of certain paraffins can be estimated. By a comparison of the entropies at 298° K. of several saturated and corresponding unsaturated organic compounds an average decrease of 2.7 electric units per mole of hydrogen withdrawn was found. Subtracting from the entropy of the hydrogen formed ($S_{298 \cdot 1} = 31.23$ entropy units, *6*), $\Delta S_{298} = 31.2 - 2.7 = 28.5$ entropy units, an average value for the entropy increase of dehydrogenation somewhat higher than the value $\Delta S_{298} = 24.6$ calculated from equilib-

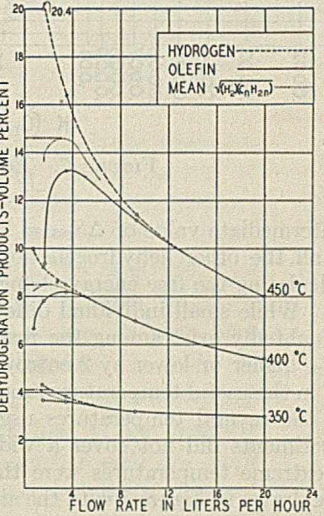


Figure 6. Dehydrogenation of n-Butane

Table III. Equilibrium Constants Calculated from Analyses

K	Temperature 350° C. (623° K.)	400° C. (673° K.)	450° C. (723° K.)	500° C. (773° K.)	600° C. (873° K.)	650° C. (923° K.)	700° C. (973° K.)
$\frac{(C_2H_4)(H_2)}{C_2H_6}$	......	0.00015	0.00076	0.0032	0.031[a]	0.082[a]	0.20[a]
$\frac{(C_3H_6)(H_2)}{C_3H_8}$	0.00038	0.0022	0.0074	......	......	......	......
$\frac{(CH_3CH_2CH:CH_2)(H_2)}{CH_3CH_2CH_2CH_3}$	0.00045	0.0022	0.0075	......	......	......	......
$\frac{(trans\text{-}CH_3CH:CHCH_3)(H_2)}{CH_3CH_2CH_2CH_3}$	0.00083	0.0039	0.014	......	......	......	......
$\frac{(cis\text{-}CH_3CH:CHCH_3)(H_2)}{CH_3CH_2CH_2CH_3}$	0.00052	0.0025	0.0087	......	......	......	......
$\frac{[(CH_3)_2C:CH_2](H_2)}{(CH_3)_2CHCH_3}$	0.0017	0.010	0.042	......	......	......	......

[a] Pease (*12*).

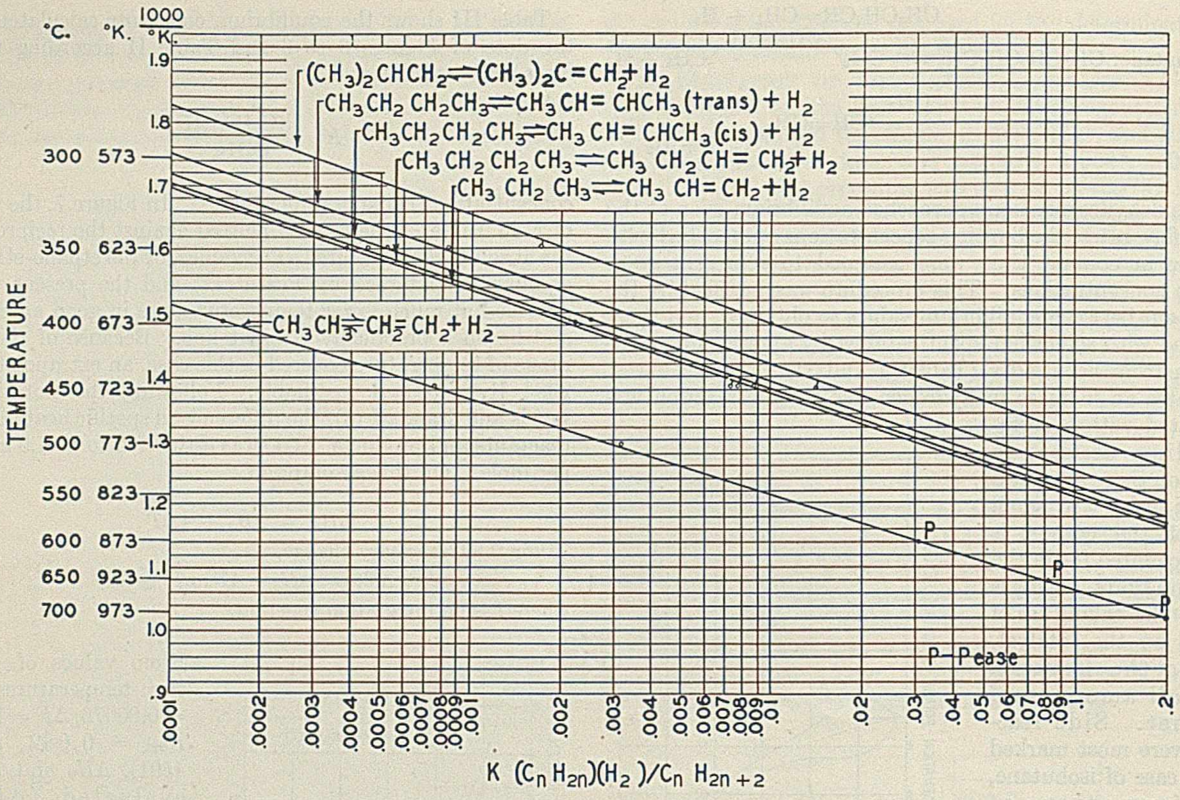


Figure 7. Equilibrium Constants

rium data for ethane. An intermediate value of $\Delta S_{298} = 27$ was arbitrarily assumed for all the other dehydrogenations studied for the purpose of calculating the free energy change over a range of temperature. While small individual differences in entropy change undoubtedly exist among the reactions studied, a value of ΔS_{298} higher or lower by 2 entropy units affects the values of ΔF in the useful temperature range only slightly. Inasmuch as the several temperatures used for the dehydrogenation experiments did not cover a wide range, and the data at the extreme temperatures were the least accurate, the curves were drawn in Figure 7 with the aid of the foregoing equations to accommodate the best single experimental value of K, assuming ΔC_P equal to 4.0 calories and ΔS_{298} equal to 27, for propane, *n*-butane, and isobutane. It is not thought that the displacement of any experimental values of K from the curves exceeds the experimental error. This method of calculation may involve large errors in ΔH and ΔF at 298° K., but the error in ΔF is probably in no case more than several hundred calories at temperatures of 573° to 873° K. (300° to 600° C.) where these reactions are of importance. The data are for the most part correct and comparable within narrower limits than this.

Ethane, Propane, and Isobutane. From the data of Pease the free energy change of the dehydrogenation of ethane at 298° K. was calculated by Parks and Huffman (*10*) to be 22,600 calories. This value is confirmed by the present data. In the dehydrogenation of propane to propylene a somewhat lower free energy change takes place (Table IV). This appears to be due mostly to an increase in stability of the ethylene molecule caused by the substituent methyl group. The free energy change is still lower for the formation from isobutane of isobutylene, an unsymmetrical dialkyl ethylene (Table IV). In the dehydrogenation of isobutane, no *n*-butene was formed, and evidently no rearrangement took place.

n-Butane. In the dehydrogenation of *n*-butane, all three of the known isomers—1-butene, *cis*-2-butene, and *trans*-2-butene—were formed. For the determination of the individual isomers, 40 to 80 grams of *n*-butane were passed over the catalyst, and the butenes separated and analyzed by the method described in the analytical section. Low flow rates were chosen to allow all the dehydrogenation reactions to come practically to equilibrium. The data are shown in Table II. That the equilibrium proportions of the three butenes were produced is shown by the hydrogenation of a mixture of 1-butene, hydrogen, and *n*-butane (Table II, experiment 2). The proportion of each butene is substantially the same as in the case of the dehydrogenation experiments. While the equilibrium concentrations were not quite attained except at the lower temperature by reason of loss in activity of the catalyst during protracted use, the similarity in the several analyses indicates that this loss in activity did not affect the proportions of products appreciably.

Table IV. Free Energies of Dehydrogenation

	ΔF	ΔF at 673° K. (400° C.)
$C_2H_6 \rightarrow C_2H_4 + H_2$	$27{,}798 - 9.21T \log_{10}T + 2.17T$	11,730
$C_3H_8 \rightarrow C_3H_6 + H_2$	$25{,}920 - 9.21T \log_{10}T - 0.21T$	8,250
n-$C_4H_{10} \rightarrow C_2H_5CH{:}CH_2 + H_2$	$25{,}790 - 9.21T \log_{10}T - 0.21T$	8,120
n-$C_4H_{10} \rightarrow$ *cis*-$CH_3CH{:}CHCH_3 + H_2$	$25{,}580 - 9.21T \log_{10}T - 0.21T$	7,910
n-$C_4H_{10} \rightarrow$ *trans*-$CH_3CH{:}CHCH_3 + H_2$	$25{,}090 - 9.21T \log_{10}T - 0.21T$	7,420
iso-$C_4H_{10} \rightarrow (CH_3)_2C{:}CH_2 + H_2$	$23{,}900 - 9.21T \log_{10}T - 0.21T$	6,230

1-Butene, which, like propylene, is a monoalkyl ethylene, required nearly the same free energy change for its formation by dehydrogenation as propylene (Table IV). The *cis*- and *trans*-2-butenes (disubstituted ethylenes) required less free energy than 1-butene, and are accordingly more stable. Of the two 2-butenes, *trans*-2-butene is somewhat the more stable thermodynamically. The equilibrium proportions of these three isomers should change only slowly with change in temperature. 1,3-Butadiene was also formed in small amounts. The tetrabromide from experiment 5, Table II, melted after recrystallization at 117° C. Quantities of butadiene of the order of one per cent of the butenes would be expected from the withdrawal of a second molecule of hydrogen.

Judging from these results, higher paraffins can be expected to show higher extents of dissociation at equilibrium by reason of the formation of olefins containing two or more substituent groups attached to the ethylene group. In addition, the increasing number of independent dehydrogenation reactions which a paraffin can undergo increases with molecular weight, and the extent to which the paraffin dissociates should increase accordingly.

ACKNOWLEDGMENT

The authors are indebted to G. G. Oberfell and R. C. Alden for their generous support, and to L. H. Fitch and H. J. Hepp for assistance in the analysis of complex mixtures.

LITERATURE CITED

(1) Burrell, Seibert, and Jones, Bur. Mines, *Bull.* 197, 41 (1925).
(2) Dillon, Young, and Lucas, *J. Am. Chem. Soc.*, 52, 1953 (1930).
(3) Egloff, Schaad, and Lowry, *J. Phys. Chem.*, 34, 1617 (1930).
(4) Francis, IND. ENG. CHEM., 20, 227 (1928); Francis and Kleinschmidt, Am. Petroleum Inst., *Proc. 10th Ann. Meeting*, 11, Sect. III, 93–9 (1930).
(5) Frey and Yant, IND. ENG. CHEM., 19, 492 (1927).
(6) Giauque, *J. Am. Chem. Soc.*, 52, 4816 (1930).
(7) I. G. Farbenindustrie Akt.-Ges., French Patent 637,410 (July 11, 1927); British Patent 301,402 (June 27, 1927).
(8) Lewis and Randall, "Thermodynamics," p. 173, McGraw-Hill, 1923.
(9) Oberfell and Alden, *Oil Gas J.*, 27, 142 (1928).
(10) Parks and Huffman, *J. Am. Chem. Soc.*, 52, 4381 (1930).
(11) Pease, *Ibid.*, 45, 2296 (1923).
(12) Pease, *Ibid.*, 50, 2715 (1928).
(13) Pease and Stewart, *Ibid.*, 49, 2783 (1927).
(14) Podbielniak, *Oil Gas J.*, 28, 38 (1929); 29, 235 (1930).
(15) Shepherd and Porter, IND. ENG. CHEM., 15, 1143 (1923).
(16) Tausz and Putnoky, *Ber.*, 52B, 1573 (1919).
(17) Van Wartenburg, *Z. physik. Chem.*, 61, 366 (1908).

RECEIVED July 23, 1932.

Behavior of Activated Carbon with Metallic Water-Purification Equipment

A. S. BEHRMAN AND H. GUSTAFSON, International Filter Co., Chicago, Ill.

It has been found that a relatively high potential difference is set up between a bed of activated carbon and the metallic water-purification equipment in which the carbon is used. This behavior is not exhibited by wood charcoal or other carbons previously employed in water purification. A dielectric lining is now provided for such metallic equipment in order to avoid injury to the carbon, contamination of the water, and eventual destruction of the metallic equipment. Typical comparative data are given showing the potential differences set up between various types of carbons and a number of metals. The suggestion is made that there may be a relationship between the potential differences set up under certain conditions and the activity of carbons in some types of adsorption phenomena.

IN THE early part of 1929 the writers' organization began actively the commercial development in this country of the use of granular highly activated carbon for water purification, primarily for the removal of objectionable tastes and odors. It was natural that the first commercial units designed for the purpose should follow the design and construction of the conventional pressure sand filter, with the sand replaced by granular activated carbon.

Two weeks after the first installation of this sort was made in Chicago, it was reported that the effluent water from the activated carbon purifier contained an appreciable quantity of ferric hydroxide. Although this report was somewhat annoying, no special concern was felt at the time, since it was believed that the source of ferric hydroxide could probably be accounted for by the corrosive effects of the oxygen in Lake Michigan water on the new steel tank of the purifier; and, since this water is characteristically slightly supersaturated with calcium carbonate, it was confidently felt that a protective coating would be deposited on the steel fairly rapidly, thus arresting further corrosion.

Accordingly, a second examination was made a few weeks later. The situation was fully as bad as before, if not worse. Not only was the amount of ferric hydroxide in the effluent water decidedly objectionable in itself, but it was plainly only a question of time before the carbon would be definitely injured by the coating of ferric hydroxide, and before serious disintegration of the steel shell would result.

The problem was one which obviously required a quick solution. To make matters worse, several similar pieces of equipment were on their way to various parts of the country for installation; there was no reason to expect fate to be kinder in those situations than it had been in Chicago.

CARBON-METAL TESTS

Operating on one of the "hunches" that is frequently the salvation of any research laboratory, a short section of steel pipe was filled with granular Hydrodarco (the activated carbon used by the writers' organization) and covered with Chicago city water. Electrical connections were then made from the steel and from the carbon to a sensitive millivoltmeter. The needle was deflected violently across the entire scale.

Tests with other common metals and alloys showed the same effect, though to a varying degree. In all cases the activated carbon was found to be cathodic to the metallic element of the couple, thus accounting for disintegration and eventual disappearance of the metal.

Other highly activated carbons were next tried, with similar results. With relatively inactive forms of carbon, however, such as the wood charcoal and bone black previously employed in water purification, no potential difference could be detected.

In Table I are shown the potential differences observed between various types of carbons and a number of different metals and alloys. The apparatus used in making these measurements consisted of a specially prepared electrode of the carbon being tested, a plate or rod of the metal, and a sensitive voltmeter. The carbon electrode comprised a slotted hard-rubber tube (taken from the positive element of an Exide Ironclad storage battery) filled with particles of the carbon, thoroughly washed, and screened uniformly through

10 to 14 mesh (screen openings 1.65 and 1.29 mm., respectively). These tubes are $^5/_{16}$ inch (0.79 cm.) inside diameter and were used in 5-inch (12.7-cm.) lengths. After stoppering the bottom end of a tube, the tube was filled within a half inch (1.27 cm.) of the top by adding successive small portions of the dry granular carbon, lightly tapping the tube after each addition. The electrode was then immersed in water to a depth of 1.5 inches (3.81 cm.), and allowed to become thoroughly saturated. The metal electrode, likewise submerged in the water to a depth of 1.5 inches (3.81 cm.), was placed 1 inch (2.54 cm.) from the carbon electrode and connected to one side of the voltmeter.

Just before making a reading, the half inch of free space in the upper portion of the carbon electrode tube was quickly filled with dry carbon, and the tube was tapped to compact the carbon and to remove any air bubbles. The circuit was then completed by means of a brass rod, one end of which was placed in contact with the carbon, the other end being connected to the voltmeter. The purpose of these precautions was obviously to insure a dry contact between the carbon and the brass connector, and so avoid the danger of the deceptive readings which would have been obtained if the brass had come in contact with the electrolyte.

The wood charcoal and bone black used in these experiments were good commercial grades of these materials. Of the activated carbons employed, Hydrodarco is prepared by processing certain Texas lignites; and Nuchar is made from certain cellulosic residues in the paper industry. Minchar is prepared by the destructive distillation of a carbonaceous shale. Only these carbons are included in the accompanying tables, as certain comparative data concerning them have already appeared in the literature (*2*); but other carbons have been similarly studied.

TABLE I. VOLTAGES OF VARIOUS CARBON-METAL COUPLES

CARBON	ELECTROLYTE	METAL								
		Steel	Brass	Monel	Cast iron	Cu	Zn	Al	Pb	Stainless steel
Hydrodarco	1[a]	0.12	0.06	0.09	0.13	0.05	0.19	0.21	0.15	0.09
	2[b]	0.14	0.06	0.10	0.15	0.05	0.21	0.26	0.17	0.10
Nuchar	1	0.08	0.04	0.05	0.09	0.02	0.14	0.14	0.11	0.05
	2	0.08	0.04	0.06	0.09	0.03	0.16	0.17	0.12	0.06
Minchar	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bone black	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	2	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00
Wood (maple) charcoal	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

[a] Chicago city water (total solids, 150 p. p. m.; pH 7.9).
[b] Chicago city water plus 350 p. p. m. NaCl (pH 7.8).

The values of the potential differences given in Table I are relative rather than absolute; it is entirely possible that refinement of the procedure employed would slightly modify these results. For the purpose of the inquiry at hand, however, it is felt that these data are amply accurate.

PHENOL ADSORPTIVE CAPACITY OF CARBONS

The question then arose as to a possible connection between the potential difference developed in galvanic couples of the sort described and the activity of the various carbons as measured in other ways. Since one of the most useful characteristics of activated carbon in water purification is its ability to remove phenols, chlorophenols, and other phenolic derivatives, the effort was made to determine whether or not the phenol adsorption capacity of a carbon could be related to the potential difference set up between itself and a metal in contact with water or stronger electrolyte. Here again the procedure followed was one chosen for its convenience and rapidity in giving results of relative value, rather than the cumbersome (and in this case not so practical) method ordinarily followed in plotting the so-called adsorption isotherm (*1*). The method employed consisted essentially in allowing a solution containing an excess of phenol to percolate through a bed of granular carbon under carefully controlled conditions, and then in determining the residual phenol in the effluent. The aqueous solution of phenol used contained 250 mg. per liter. The carbon bed had a depth of 6 cm. and a volume of 32 cc. As before, the carbon was screened through 10 to 14 mesh, and was thoroughly washed before use. One liter of the phenol solution was passed through the carbon bed in just 30 minutes, the flow being controlled by means of a calibrated orifice. The adsorption capacities of the various carbons tested are given in Table II.

TABLE II. PHENOL ADSORPTION CAPACITY

CARBON	PHENOL REMOVED BY 32 CC. CARBON	CARBON	PHENOL REMOVED BY 32 CC. CARBON
	Mg.		*Mg.*
Hydrodarco	195	Minchar	12
Nuchar	127	Wood charcoal	9
Bone black	43		

DISCUSSION OF RESULTS

It is evident that there is a striking parallelism between the magnitude of the potential difference set up by a carbon with a metal, and the adsorption capacity of that carbon for phenol. If the behavior of carbons in other respects exhibits a consistent relationship of this sort, the thought suggests itself that the magnitude of the potential difference set up under certain control conditions might be taken as a crude measure of, or index to the activity of a given carbon. Not enough data are available at this time to do more than suggest this possibility.

Based on the work described in the foregoing and upon other related investigations, a patent application was filed covering metallic water-purification equipment, employing a bed of activated carbon in which a nonconducting lining is inserted between the carbon and the metal. Shortly after this application was filed, a patent on the same subject was issued to Brandt (*3*) of the Darco Corporation. It is all too common, in industrial research and development, to find one's work and results anticipated by some other investigator. The present case is unusual in that Brandt's organization was already associated with that of the writers', so that the fruits of both investigations could be combined commercially, even though there had been unknowingly and unintentionally an appreciable duplication of effort and expense.

Another method of overcoming the destructive galvanic action described in the foregoing is to apply a small counter-electromotive force. A description of this method (which is covered by a pending patent application) and results obtained with its use are reserved for presentation in a future paper.

LITERATURE CITED

(1) Bancroft, "Applied Colloidal Chemistry," p. 28, McGraw-Hill, 1921.
(2) Baylis, *J. Am. Water Works Assoc.*, 21, 789 (1929); Norcom and Dodd, *Ibid*, 22, 1415 (1930).
(3) Brandt, U. S. Patent 1,781,314 (Nov. 11, 1930).

RECEIVED June 2, 1932. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 83rd meeting of the American Chemical Society, New Orleans, La., March 28 to April 1, 1932.

Sugar Industry in Foreign Lands

C. A. Browne, Bureau of Chemistry and Soils, Department of Agriculture, Washington, D. C.

An account is given of observations upon the agriculture, chemistry, technology, and economics of sugar production in various countries which were visited by the author in 1929 and 1930. Conditions in England, Germany, France, Spain, Czechoslovakia, and Egypt are described.

During an agricultural-chemical tour of sixteen months which the writer made in 1929 and 1930 through various countries of Europe and the Near East, considerable attention was devoted to observations upon the chemistry, agriculture, technology, economics, and history of sugar production. In the present paper only a brief résumé can be given of some of these observations, as a complete review of all the information that was gathered would greatly exceed the limits of the present paper.

In all the countries that were visited there was a general state of agricultural and industrial depression, similar to that existing in the United States. There was the same talk of the overproduction of sugar and other agricultural commodities; there was the same existence, in varying degrees, of unemployment; and there was the same agitation about tariffs, taxes, subsidies, and other measures of relief. Time is lacking to discuss these economic remedies, many of which when put into effect had results that were not anticipated by their proponents at the beginning. In Egypt, for example, at the time of my visit the announcement of an increase in the tariff upon sugar had the result of stimulating immediate importations of thousands of tons of this commodity before the proposed new law went into effect. The warehouses of Alexandria were glutted with sugar, far exceeding the immediate needs of consumption, from the sale of which afterward the government derived not a particle of the increased revenue and for the purchase of which the consumer had to pay the subsequent increase in price. The sugar speculators profited greatly by these developments, but the sugar manufacturers of Egypt, whom the new law was supposed to protect, suffered a temporary loss from the invasion of their markets with a flood of cheap foreign sugar.

BEET SUGAR INDUSTRY

England

The beet sugar industry of England is one of those interesting new developments which have taken place since the World War. The old established policy of free trade, under which Great Britain exchanged the products of its mines and factories for its supplies of foodstuffs and raw materials, is now giving way to a policy of protection and of encouraging hitherto neglected industries. This new departure, like similar nationalistic movements in other countries, has for its purpose the strengthening of domestic manufactures and the rendering of the nation less dependent upon the outside world in the event of future commercial or political disturbances.

Beet sugar manufacture in England was encouraged in the beginning by the granting of governmental subsidies, which were to be gradually diminished as the industry approached a self-sustaining basis. This latter condition, because of the general world-wide depression in the sugar markets, has not been realized; if the new beet sugar industry of England is to withstand the competition of cheap tropical sugar, it can do so only upon a continuance of the subsidy or by means of tariff protection.

Certain technological difficulties have also had to be surmounted in England. The most important of these has been the devising of means to prevent the pollution of streams and the killing of fish by effluent waters. The rivers of England are small and hence incapable of receiving so large a volume of contaminating wastes as the large streams of the United States and Europe. This difficulty has been overcome by reducing the quantity of waste waters from the sugar factories by an improved process of diffusion and also by devices for filtering and purifying the effluents before their discharge into the rivers.

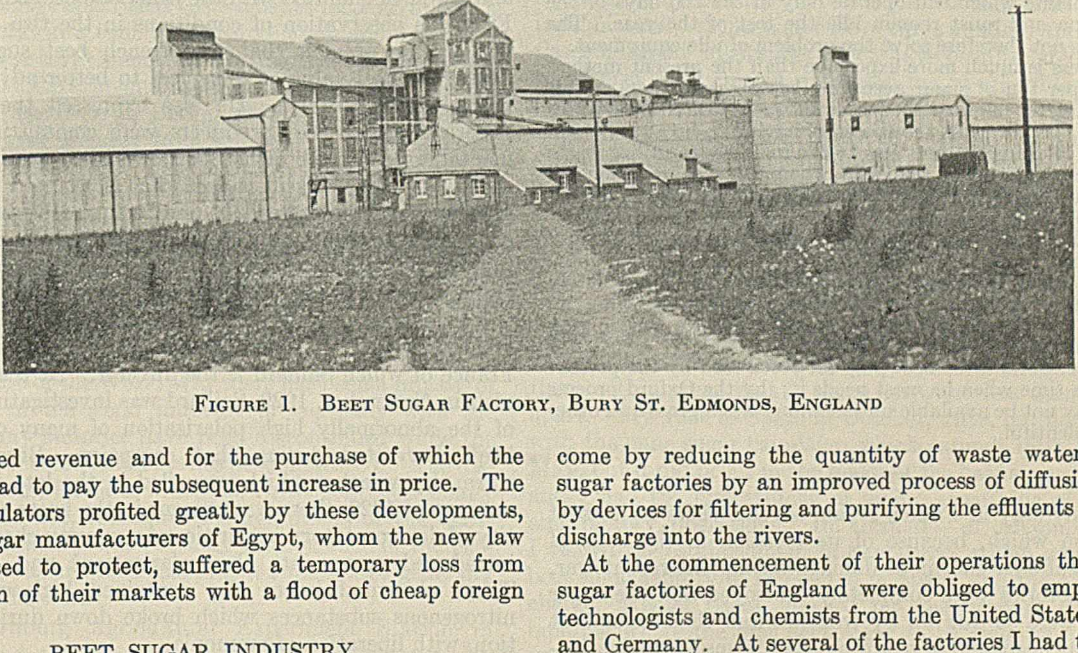


Figure 1. Beet Sugar Factory, Bury St. Edmonds, England

At the commencement of their operations the new beet sugar factories of England were obliged to employ foreign technologists and chemists from the United States, Holland, and Germany. At several of the factories I had the pleasure of meeting fellow Americans. The training of a large body of competent British technologists was one of the first problems of the new beet sugar industry in England. This is highly desirable, as foreigners are not always sympathetic with

British traditions. Foreign superintendents are also prone to appoint relatives and friends to important positions and thus there is the same danger, which our American beet sugar industry encountered several generations ago, of receiving a foreign and not a domestic type of development. I visited four of the eighteen beet sugar factories of England—Selby, Colwick, Bury St. Edmonds, and Ely.

In addition to these four factories, I also visited the experimental beet sugar factory at Eynsham, near Oxford, where technological researches have been conducted for a number of years upon the desiccation of sugar beet cossettes and the manufacture of sugar therefrom by the Oxford or modified De Vecchis process (*5*). The chief advantage claimed for this system is that it enables the factory to operate with dried cossettes during the whole year and not for only a few months as is required by the usual method of diffusing the freshly sliced beets. It was generally held by the sugar technologists whom I visited in the various countries of Europe that the losses from increased fuel consumption and other causes by the new process more than outweighed the advantages of continuous operation. The experiments attracted visitors from all parts of the world, but have now been discontinued. The following are a few of the objections that were advanced by foreign technologists against the Oxford process:

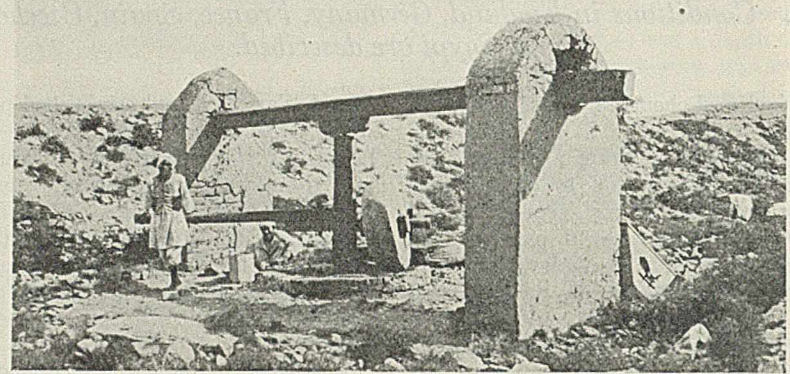


FIGURE 2. STONE EDGE-RUNNER MILL

This type was formerly used for grinding sugar cane, and is still used in the Orient for crushing olives, ore, and other substances.

> The process involves a large expenditure of capital for dehydrating plants which can operate only in the 100 days of the slicing season and must remain idle the rest of the year. The process does not therefore solve the problem of idle equipment.
>
> The process is much more expensive than the present method (£ 4 more per ton of sugar according to one statement). This is due partly to the increased cost of evaporation (the water removed in dehydrating the cossettes having to be added again at the time of diffusion) and also to the inability to utilize waste steam as perfectly as in processes where all the operations of slicing, diffusing, evaporating, crystallizing, etc., are conducted in one establishment.
>
> The dried cossettes are bulky and will require a large amount of extra storage space.
>
> Beets are made into sugar which can be marketed immediately by the present method; there is the possibility of tying up capital by the Oxford process in stored cossettes which may undergo deterioration.
>
> The farmer obtains his beet pulp for stock feed by the present method at a time when he most needs it; by the Oxford process the pulp may not be available until summer when grass and other forage are plentiful.

FRANCE

During my stay in France I paid several visits to its beet sugar region which, because of its location in the zone of hostilities, suffered enormous damage during the recent war. Scores of factories were completely destroyed and the sugar beet fields were so dug up by trenches and shell holes that many owners despaired of restoring their farms to productiveness. Few things impressed me so much during my whole trip as the thoroughness and completeness of this work of restoration. Entirely new factories have been erected to replace those destroyed and in this one respect the war has been a benefit, for many of the old beet sugar establishments of France were obsolete and the costs of modernization were charged up against the invader.

The damage to the beet fields was far greater than that to the factories. Buildings and equipment can be replaced at short notice, but to restore a war-damaged field to its former productiveness requires not only the labor of removing debris, leveling earthworks, and filling trenches, but also that of intensive manuring and cultivation over a long period of time. I saw some of this work of field restoration, and, although most of it has now been accomplished, it will be many years before the last scars of the war have been obliterated.

The beet sugar estate of Guignicourt which I visited was situated in a most exposed region near Reims, directly between the two hostile lines, and its owner, M. Barbarre, president of the Comité Central des Fabricants de Sucre de France, informed me that the chaos of destruction which met his eyes after the close of the war almost caused him to abandon the hope of reëstablishing his business. As he escorted me through his new model factory with fine up-to-date equipment he remarked that in looking back upon the past it seemed to him as if two impossibilities had occurred—the impossibility of making so complete a scene of wreckage and the impossibility of making so thorough a restoration.

At Guignicourt I had the pleasure of meeting also M. Barbarre's son, Pierre, who has visited the United States and is well acquainted with the American beet sugar industry. From his observation of conditions in the two countries he was of the opinion that the French beet sugar factories utilize the fuel value of their coal to better advantage than in the United States. He also expressed the belief that American sugar beet producers were committing a fundamental error in not growing their own sugar beet seed. They should develop, he said, a seed that is adapted to American soils and climate instead of purchasing seed from European growers who study only their own peculiar conditions. A full description of the new restored beet sugar factory at Guignicourt has been published by Saillard (*10*).

I paid several visits during my residence in Paris to the laboratories of the Comité Central des Fabricants de Sucre de France of which Saillard is the director. At the time of my visit in November, 1929, Saillard was investigating the cause of the abnormally high polarization of many of the sugar beets harvested during that campaign. Because of the warm dry weather which prevailed in the late summer and autumn of 1929, there was present in the beets a large quantity of dextrorotatory impurities of a gummy character which introduced errors into the polarizations and calculations. These abnormal juices also contained high quantities of nitrogenous substances which broke down during evaporation, with liberation of ammonia.

GERMANY

Shortly after my arrival in Europe I began to hear rumors of a new machine for setting out the young plantlets, or

Stecklings, of sugar beets—a machine that, according to the prophecies of some enthusiasts, was destined to revolutionize the agriculture of the sugar beet by diminishing the costs of labor. I was informed, however, by Schneider of the well-known sugar beet seed establishment at Kleinwanzleben that this method of transplanting *Stecklings* would never become general. The breaking off of delicate rootlets of the young plants by the machine causes the development of deformed beets with forks and prongs which not only enclose dirt during harvesting but increase greatly the difficulties of manufacture.

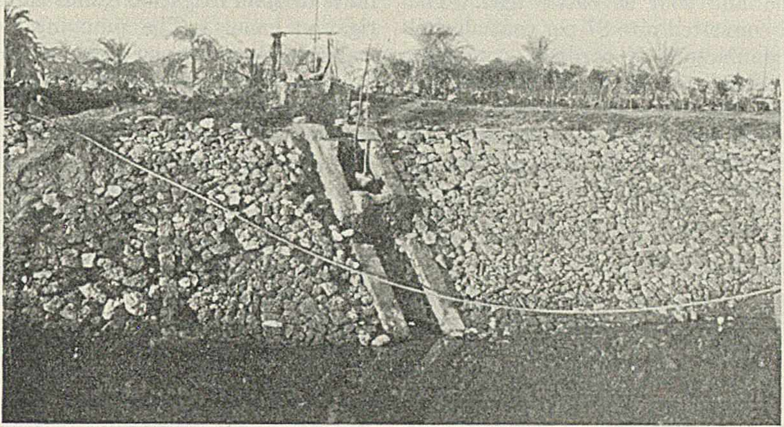


Figure 3. Primitive Water Sweeps, or *Shadufs*, for Irrigation, Asyut, Egypt

During my visit at Kleinwanzleben I witnessed the testing of mother beets for seed propagation. The processes of boring, weighing out, digesting, clarifying, making to volume, filtering, and polarizing are carried out with the greatest celerity. Five chemists, with two helpers at the boring machine, are able to test as many as two thousand beets in a day. In the early days the specific gravity of the plug that was bored from the mother beet was the index of selection, and it was not until the invention of the polariscope that the present method was introduced.

The present period of industrial depression and low prices has had its natural effect in Germany and elsewhere in directing research toward the introduction of all sorts of new economies. The extraction is not being pushed to the greatest attainable limits as in the days of high prices. It is the last half per cent of sugar that costs most to recover, and it is therefore natural in a time of overproduction and low prices that more of the sugar should be left unextracted in the pulp and molasses. Experiments were being conducted at the famous Sugar Institute in Berlin, at the time of my visit, upon the removal of sugar from the beet by expression, instead of by diffusion, which is a return in principle, but with modern improvements and modifications, to the original process of Achard.

One of the most important recent improvements in sugar factory control that came to my attention in Europe was the new Zeiss vacuum pan refractometer which gives the solid content of the sirup in the pan directly with temperature correction at any moment of boiling.

Since the close of the World War there has been a process of centralization in the sugar industry of Germany with the result that many factories have been discontinued while the capacity of other establishments has been increased. The dismantled beet sugar factories which the visitor sees occasionally in Germany are not, therefore, the symptoms of the decadence of the industry but are only an evidence of the economic reorganization which has affected industries generally in all parts of the world.

At the Bernburg Agricultural Experiment Station in Germany I had the pleasure of meeting its director, W. Krüger, whose scientific career of over fifty years has been associated with agricultural research upon sugar-producing plants, first upon the sugar cane in Java as director of the Kagok Experiment Station and then upon the sugar beet as director of the Bernburg Station in Germany. Krüger's early work on sugar cane (*7*) brought him wide recognition, but even more famed is his latest book on the sugar beet (*8*). Director Krüger showed me his extensive pot and field experiments with sugar beets. He has made a most exhaustive study of the abnormalities in the color and form of sugar beet leaves, produced by diseases, by parasites, and by deficiencies of nitrogen, phosphoric acid, potash, lime, and other fertilizing constituents of the soil—a branch of agricultural science known as foliary diagnostics. A glance at a field of growing sugar beets was sufficient for Krüger to indicate what elements of plant food were lacking.

Another experiment station visited in Germany, where tests were being made upon the growing of sugar beets, was that at Limburger Hof which is owned by the I. G. Farbenindustrie Gesellschaft. This is probably the best equipped and most diversified agricultural experiment station in the world. In the greenhouses of this station, which are provided with devices for temperature and humidity control, I saw to my great surprise fertilizer experiments being conducted upon the sugar cane and other tropical plants.

Czechoslovakia

While in Czechoslovakia I paid a visit to the Sugar Institute of Prague where chemical research work of the highest order is being conducted upon the sugar beet and beet sugar manufacture. A museum case of three hundred and fifty bottles, containing substances which have been isolated from the sugar beet, particularly impressed me as an evidence of the painstaking research spirit of the chemists of this station. Experiments were being conducted here at the time of my visit upon the use of the photoelectric cell in the colorimetric and polarimetric examination of sugar solutions. Time is lacking to give an account of this and other lines of research that were explained to me during my visit.

Spain

Spain is a country of unique interest to the sugar technologist, as the sugar cane and sugar beet are both cultivated there within areas that in some cases are less than 50 miles apart. My visit to Spain in October, 1929, did not coincide with the cane sugar campaign which extends from March to May, but it did occur in the midst of the beet sugar campaign and I had the opportunity of seeing something of the field and factory operations. In Granada, of Alhambra fame, I visited the establishment of San Isidro, which was the first beet sugar factory to be erected in Spain, and the engineer in charge, Miguel Lacal, showed me the original diminutive building where the first beet sugar to be made in Spain was crystallized. The beet sugar campaign in the region of Granada lasts from July to December. The beets mature early on the low plains where harvesting first begins, and then, as the campaign advances, the beets are dug from the more highly elevated fields on the lower slopes of the Sierra

Nevada mountains. The wide range of climatic conditions within a narrow area is thus favorable to a long campaign.

The machinery employed at the San Isidro factory is of French and German construction. A high-grade sugar is manufactured which is washed well and then steam-cured in the centrifugals. The concrete of pure white sugar is then removed as broken concave pieces which are ground up into granulated sugar and packed in 60-kg. sacks for shipment. The low-grade products are remelted and recovered as first sugar. The pulp is dried and sold as cattle feed. The molasses is fermented and converted into 87 per cent alcohol which is sold for the manufacture of cordials, perfumes, chemicals, and other industrial products. Lacal took me through the factory, distillery, pulp-drying rooms, warehouses, lime ovens, laboratory, yards, and other parts of the establishment which for its good order and excellence of equipment presents a most favorable appearance.

SUGAR CANE INDUSTRY

Early Arab Mills

Sugar cane was first introduced into the Mediterranean countries by the Arabs in the seventh century A. D. The oldest evidences of the Arab cane sugar industry which I saw were the ruins of an ancient factory near the remains of the Biblical city of Jericho in Palestine. These ruins of the old evaporating house and other buildings are now tenanted by a Bedouin who pointed out to me the vestiges of the aqueduct which once supplied water to the mill. This factory was in operation at the time of the Crusades, and the present ruins have an antiquity, therefore, of more than 700 years. Sugar cane is still grown in the plains of Jericho but only for purposes of eating.

The type of mill used in these early Arab cane sugar factories was probably of the vertical stone edge-runner type such as is used very generally in the Mediterranean countries at the present time for crushing olives, oily seeds, and other products. This form of mill was used in Spain for crushing sugar cane and was introduced at an early date into the American colonies. The stone edge runner for grinding cane was succeeded at a later date by vertical rollers, such as may be seen at the present time in some of the primitive tropical mills that are operated by wind or animal power.

Egypt

Irrigation. The greater part of Egypt is without rain, and the cultivation of sugar cane in this country would be impossible without irrigation. Water is supplied to the fields from the Nile and the irrigation canals by a variety of methods. The first of these is the ancient *shaduf*, or water sweep, operated by man power. In some cases where the fields are high above the water there may be as many as four tiers of these *shadufs* one above the other. This primitive appliance has come down unchanged through many thousands of years from the time of the ancient Egyptians.

Another primitive but more efficient irrigation device employed everywhere in Egypt is the *sakia* which consists of a vertical windlass supported upon a crude framework of timber and operated by oxen, camels, or donkeys. An endless rope of woven fibers bearing a series of earthen jars or buckets descends from the windlass to the level of the river, from which the water is elevated and emptied into the irrigation canal at the top where it is diverted by lateral ditches into the fields.

Almost side by side with these ancient irrigation devices the visitor in Egypt may see boiler houses with steam centrifugal pumps which will supply more water in a minute than a man with a *shaduf* can lift in a day.

At the present time the irrigation facilities of Egypt are being doubled by raising the great Aswan dam an additional 30 feet. This will permit the perennial irrigation of land that hitherto has only been watered by the overflow of the Nile at the time of flood, and also the recovery of some hundred thousand acres of good land in the Nile Delta which requires only the elimination of accumulated salts by irrigation with fresh water to be brought to a state of fertility.

The extent of the irrigation developments on some of the large estates in Egypt is enormous. At the Kom-Ombo estate, which I visited in February, 1930, there are over 110 miles of main irrigation canals and 180 miles of secondary irrigation canals. The pumping station for supplying this water is situated upon the banks of the Nile into which dip the four large intake pipes; through these pipes the water is pumped at the rate of 14 tons of water per second into the main irrigation canal. The silt which is constantly being deposited by the Nile water must be removed by dredges; otherwise, it would speedily impede the operation of the canals. This silt has considerable fertilizing value and is spread upon the land.

I was informed at Kom-Ombo that 400 cubic meters or tons of irrigation are needed to produce one ton of sugar cane between the times of planting and harvest. This means that about 3600 tons of irrigation water are needed to produce one ton of sugar; thus one can form an idea of the immense demands of a crop for water in an arid climate such as Upper Egypt where it rarely rains.[1] The greater part of this water is lost by evaporation and never reaches the crop. The Nile water carries in solution about 200 p. p. m. of calcium bicarbonate, sodium chloride, and other soluble salts which would be left as harmful saline residues in the soil were they not prevented from accumulating. One can see in many places in Egypt a white efflorescence or crust of salts upon the soil where the dissolved saline residue has been brought to the surface by capillarity. The reactions which this mixture of salts undergoes in the sandy clay alluvium are of a complicated character. Sodium carbonate is formed, a type of reaction familiar to every soil chemist, and the soil in consequence is rendered alkaline. For the removal of this and other noxious saline constituents of the soil, a thorough system of drainage must be established in connection with that of irrigation. The Kom-Ombo estate has 199 miles of drains and a main drainage canal 14 miles long.

Cane Sugar Production at Kom-Ombo. The Kom-Ombo Company has approximately 30,000 acres of land under cultivation, of which 8000 acres are devoted to wheat, 7500–8000 acres to sugar cane, 5000 acres to maize, 2500 acres to cotton, and 1000 acres each to alfalfa, sesame, and barley. For the operation of so vast an enterprise a large amount of equipment is required. The total length of plantation railways is nearly 150 miles. At the time of my visit the Kom-Ombo Company owned 25 locomotives, 699 plantation cars, 25 Fowler plows, 322 oxen, 195 asses, 29 camels, and various other equipment too numerous to mention. The total population upon the Kom-Ombo domain is about thirty thousand of which some twenty thousand actually perform labor.

The cane planting had just begun at Kom-Ombo at the time of my visit. In preparing the land, Fowler engines are used for operating the cables that draw the plows. After plowing, the fields are harrowed and then divided into furrows about 31 inches apart. The cane is planted in furrows, the bottoms of which are about 15 inches below the top of the dividing ridge. The cane used for planting is freshly cut and brought

---

[1] Experiments conducted in Hawaii and elsewhere show that about 300 pounds of water are transpired by the sugar cane in the production of one pound of sugar. Only a small part of the water supplied to a cane field by rain and irrigation is actually taken up by the crop, the larger part being lost by evaporation and drainage. In Hawaii it has been estimated that about 1000 pounds of water must be supplied to produce one pound of sugar. In Egypt where evaporation is more intense, the proportion of water to sugar is necessarily much higher.

immediately by camels to the place of planting where it is divided into sections of four or five joints. Two rows of cane are laid side by side in the furrow, with the sections overlapping and the buds upon the side (not on the top or bottom). The cane is then covered to a depth of 3 or 4 inches by earth hoed from the bottom of the adjoining furrow which is then planted in its turn. The fields must be irrigated within 24 hours after planting, and the water is turned in again every 14 or 15 days. In the hot summer the interval between the applications of water is reduced to 12 days. Irrigation is suspended entirely 20 days before cutting. About 4 months after planting, the cane is laid by, the earth between the rows being turned and banked up against the growing cane.

The total amount of sugar cane ground per year at Kom-Ombo is at present about 300,000 tons. The chief variety cultivated, making up 80 per cent of their planting, is a Java seedling, known as No. 105, of the slender, light colored Uba type. It gives a yield per acre of 40 to 50 tons and has a sucrose content of 12.5 to 13.5 per cent at the time of harvest. The remaining varieties consist of a purple cane, called the Baladi, giving a yield of only 20 to 25 tons per acre but with a sucrose content of 13 to 14 per cent; the Rubanee, or ordinary striped or ribbon cane, of the same yield and sugar content as the Baladi; and a new Java seedling, No. 2714, with a sucrose content of 13 to 14 per cent, but giving a smaller yield per acre than the No. 105. It was stated by the agronomic engineer at Kom-Ombo, S. Mezrahi, that no cane had yet been found which equals the No. 105 in production of sugar per acre under the conditions of this estate.

Cane is planted at Kom-Ombo in February and March and is cut after growth of one year. It is allowed to ratoon for two years. I was surprised to learn that the first year's stubble frequently exceeds the plant cane in tonnage; this was attributed by Mezrahi to the greater development of new succors from the root buds. The cane does not arrow at Kom-Ombo; the failure to do so is attributed to the extreme dryness of the climate.

During the grinding season, sample carloads of cane from the field are taken each day to sheds where the stalks are weighed and then cleaned of adhering trash, the latter being weighed and the percentage determined. At the time of my visit the percentage of trash for the Java No. 105 cane was 2.415, and for the Baladi purple cane 1.836. These percentages, as determined each day for the sample loads, were applied to the total amount ground at the factory, which was about 2500 tons per day. Experiments were being tried at Kom-Ombo upon utilizing the upper green part of the cane for seed, the less valuable part of the stalk thus being used for planting, and the richer lower section, of higher sucrose content and purity, being employed exclusively for grinding.

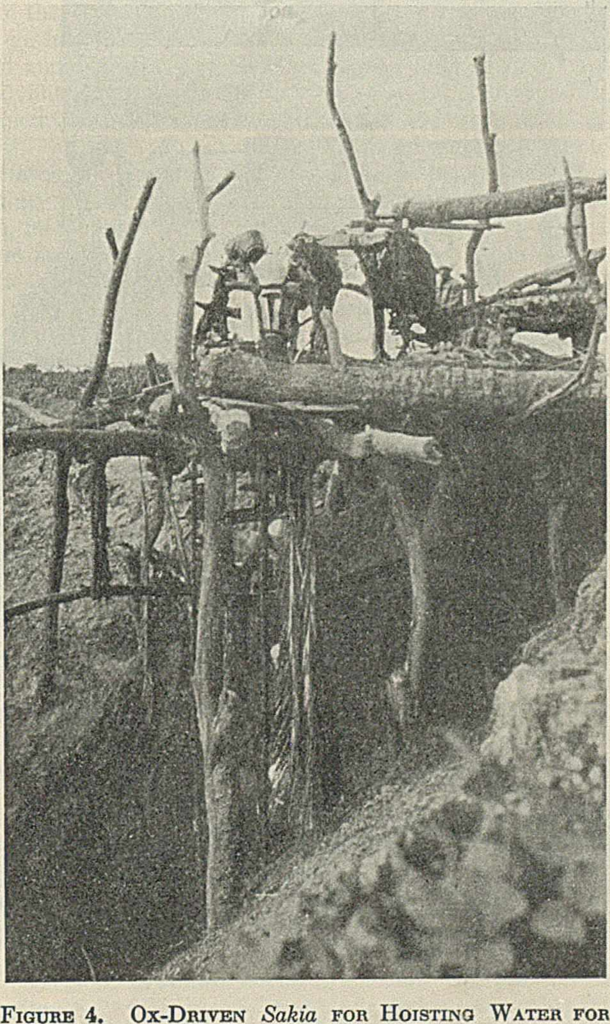


FIGURE 4. OX-DRIVEN *Sakia* FOR HOISTING WATER FOR IRRIGATION, ABU SIMBEL, EGYPT

The cars of sugar cane after arrival at the factory are unloaded according to the Stork system of Hengolo, Holland. Chains are passed through steel channels on the bottom of each car and then linked together on the top of the load of cane. The whole load of about 4 tons is then lifted by a traveling crane on to an inclined platform from which it is dragged by a large mechanical rake on to the carrier which transports the cane to the mill. Two lines of cane cars can be unloaded at the same time. Each car after unloading is run on to a movable platform that shifts it to another track from which the empty cars are hauled again to the fields. Formerly the cane at Kom-Ombo was all unloaded by hand and several hundred men were employed to do the work now performed by about twelve workers.

The cane on entering the factory is passed first through the rolls of a corrugated crusher and then through five three-roller mills (Cail manufacture). Six minutes are required for the cane to pass through the entire system of rollers. Maceration is employed and an extraction of 95 per cent was reported at the time of my visit. The bagasse is conveyed by carrier to the boilers where it is fed to the fire boxes, partly by hand and partly by mechanical stokers. The cheap labor of Egypt (a good worker can be hired at 20 to 25 cents per day) has delayed the introduction of many labor-saving devices that have been found necessary in other countries. Bagasse supplies about 90 per cent of the fuel necessary to run the factory at Kom-Ombo; oil and coal (from England) supply the remaining 10 per cent in about equal quantities. The expenditure for foreign fuel will shortly be entirely eliminated by burning the excess molasses which is left after supplying the needs of the alcohol distilleries. The nature of the proposed installation for burning molasses at Kom-Ombo is not known to the writer at present. Molasses burning for steam production, with subsequent recovery of potash from the ash, has been a subject of frequent discussion in the literature. In one type of process the molasses is thoroughly incorporated with the bagasse before burning under the boilers. When the molasses is burned alone it must be subjected to a preliminary process of charring to prevent frothing. Special precautions must also be taken to prevent slag formation from fusion of the ash (*1-4, 6, 9, 11, 12*).

The juice from the crusher and mills is first sulfured, then limed to neutrality, heated, settled, and filtered, first through bagasse and finally through Dehne filter presses. The clarified filtered juice is then evaporated in quadruple effects and boiled to grain in Cail vacuum pans. The

Figure 5. Pumping Station and Irrigation Canal, Baliana, Egypt

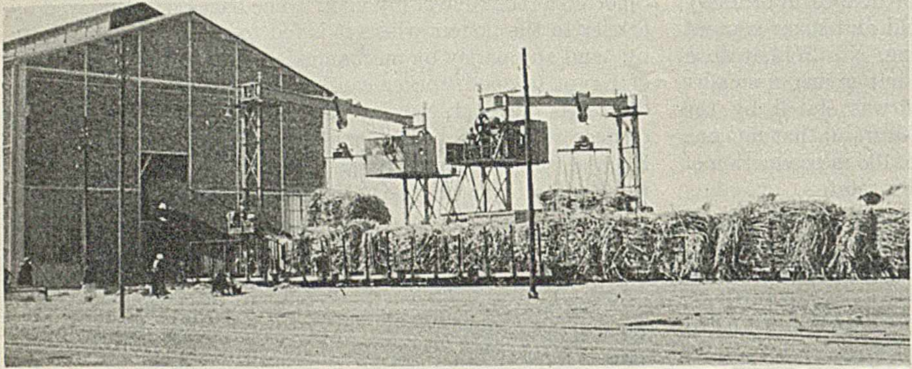


Figure 6. Cars of Sugar Cane at Factory, Kom-Ombo, Egypt

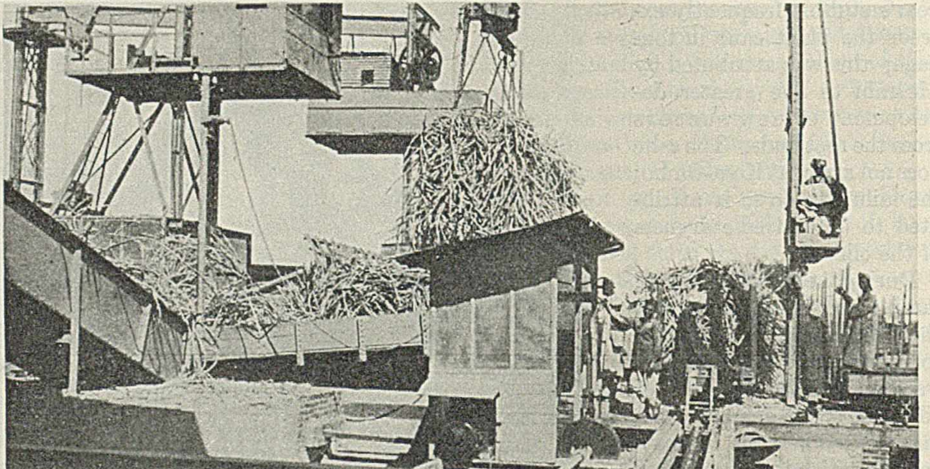


Figure 7. Transferring Sugar Cane from Cars to Carrier, Kom-Ombo Factory, Egypt

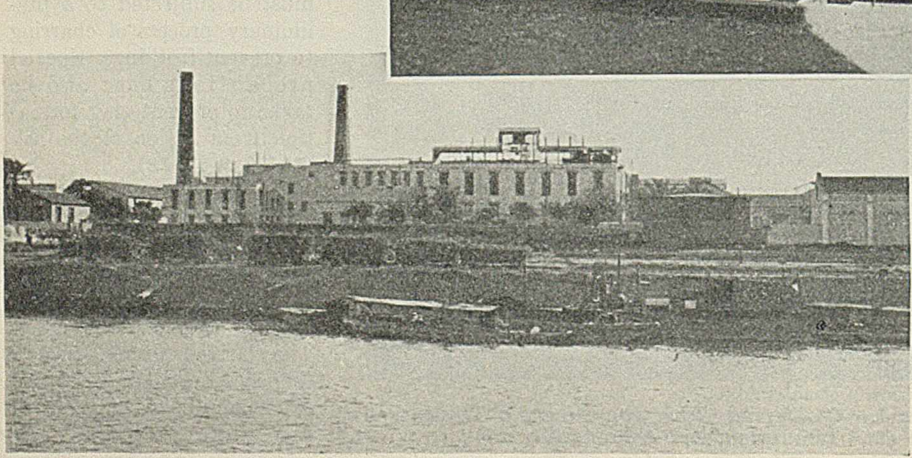


Figure 8. Cane-Sugar Factory on the Nile at Nag Hamadi, Egypt

strikes of raw sugar are purged in Watson-Laidlaw centrifugals, sixty in number, each one of which is electrically operated by an independent motor.

A high-grade white sugar of about 99.5 polarization is now the only kind manufactured at Kom-Ombo. The sugar is packed in 100-kg. bags and stored in warehouses for shipment to the refinery at Hawamdia. The molasses is stored in tanks and also in open reservoirs of banked earth, previous to being shipped to the distillery.

There were five cane sugar factories operating in Egypt at the time of my visit, these in order of production being Nag Hamadi, Armant, Kom-Ombo, Sheikh Fadl, and Abu Kirkas. All of them belong to the Société Genérale des Sucreries et de la Raffinerie d'Egypte.

SUGAR REFINING IN EGYPT. The raw sugar manufactured at the five factories previously named is sent down the Nile to the refinery of the Société Genérale at Hawamdia. Through the courtesy of H. Naus Bey, general administrative director of the Société Genérale des Sucreries et de la Raffinerie d'Egypte, I was granted the privilege of visiting this refinery which, for the variety of its operations, is one of the most interesting establishments of its kind in the world. It is picturesquely situated among groves of palm trees upon the bank of the Nile.

The Hawamdia refinery at the time of my visit (February, 1930) employed some two thousand men and was melting about 420 tons of raw sugar a day, although on occasions this figure was raised as high as 520 tons. The raw sugar received from the factories up the Nile was of very high quality (all above 99° and a large amount polarizing as high as 99.4° to 99.5°). Some of the factory sugars were, in fact, pure and white enough to go into direct consumption but most of them were remelted and refined. The Société Genérale des Sucreries finds it advantageous to produce this high grade of raw sugar, as the operations of its own refinery are thereby greatly facilitated.

The methods of refining at Hawamdia are most varied, and the visitor has the opportunity of seeing, side by side with the most modern processes, methods which have been discontinued in some other countries for half a century or more. A brief account of operations, as observed at the time of my visit, is as follows:

The raw sugar was emptied from the bags into small tanks upon trucks where it was treated with concentrated sugar sirups of increasing purity. After the sugar had stood in contact with the sirup of lowest purity for a period sufficient to dissolve the film of adhering molasses, the liquor was removed from the tank by suction and a sirup of higher purity applied. After a series of these affinations, when as much as possible of the adhering molasses was removed, the purified sugar was melted to a concentrated sirup and the suspended impurities precipitated by adding a requisite amount of albumen dissolved in warm water. The impurities, carried down by the coagulation of the albumen in the hot sugar solution, were then removed in a filter press and the filtered sirup passed through bone char filters of which I observed about eighty. The bone char was obtained mostly from France and Holland, the specimens observed being of much coarser grain than that usually employed in our American refineries.

The clarified sirup from the char filters was evaporated and boiled to grain in vacuum pans in the usual way. A certain amount of the massecuite was then run either into open coolers, where it was stirred a number of hours by rotating paddles, or else into closed rotating crystallizers whose temperatures could be regulated by water circulating through longitudinal pipes. From the coolers or crystallizers the massecuite was purged in centrifugals, which were of the Watson-Laidlaw type, each one being separately driven by its own electric motor. The sugar from the centrifugals was then pressed mechanically into slabs which, after drying in ovens, were cut into dominoes.

Another method of treating the massecuite was to run it into metal cones which, after standing for the completion of the growth of crystals, were packed into cylindrical metal baskets (ninety-six cones to the basket) and then whirled in centrifugals to remove adhering mother liquor. The cones of sugar after removal from the centrifugals were then dried in ovens and the resultant white loaves, weighing about 1800 grams each, wrapped by hand in paper sheets and then shipped out in boxes or bags. The output of the refinery at the time of my visit was 100,000 loaves per 10-hour day at thirteen wrapping tables, although this amount was raised at times to 125,000 loaves or more per day. The demand for hard loaf sugar persists among the native population of Egypt and the Soudan, as it was the first kind of refined sugar with which they became familiar and they believe such sugar to have superior quality and sweetness.

Owing to the limited capacity of the loaf sugar centrifugals at the time of my visit, some loaf sugar was also being made by the old "fill house" method. The cones, after being filled with massecuite, were placed in holders on cars which were wheeled into hot rooms where they remained a day or two for the crystals to complete their growth and then to be washed with a highly concentrated high purity sirup. This was the oldest part of the refinery installation at Hawamdia, dating back over 40 years, and it was the only survival of the ancient "fill house" in actual operation which the author has ever seen.

When crystallization and washing were completed in the hot room, the cones of massecuite were placed with the open points down in cups attached to a large system of suction pipes, and the adhering mother liquor was drawn off. After thorough draining by suction, the cones were then emptied and the loaves of sugar dried in ovens.

In addition to dominoes and loaf sugar, Hawamdia also manufactures white slabs for the use of confectioners. The massecuites are purged in Adant turbines and the resulting slabs are dried in ovens. A considerable amount of granulated sugar is also made for the use of hotels and the domestic trade. At the time of my visit the output of granulated sugar was about 120 tons per day. There is no demand in Egypt for soft refined sugars or for table sirups, and these products are not manufactured at Hawamdia.

The massecuites of highest purity are worked up into the prime quality loaf sugar which brings the highest price in Egypt, 10 pounds of such sugar at the time of my visit retailing at 10.5 piasters or 52.5 cents. The molasses from this sugar is boiled to a large grain, and the sugar thus formed, after being well washed in the centrifugals, is dried to form granulated sugar which at the time of my visit retailed according to grade at 8.5 to 10 piasters for 10 pounds. The molasses from the second strike is again boiled, with the production of lower-grade sugars which, after being affined and remelted with the raw sugars, are worked up into loaf and granulated. The final refinery molasses of about 52 per cent purity is sold to distillers for making alcohol.

The chemical control at Hawamdia is along the usual lines followed in all refineries. There are, however, several interesting modifications that were explained to me by the refinery chemist, A. M. J. Honoré, whose father for many years was a merchant in New York City. One of these modifications is the employment of the normal weight of 20 grams which is used not only at Hawamdia but at several of the sugar factories in Egypt. The saccharimeters are of Schmidt-Haensch construction and equipped with a special scale adapted to the 20-gram weight of sugar. Honoré stated that the labor of calculation is so reduced by use of the 20-

gram normal weight that a chemist after using it but once is convinced of the reasonableness and advantage of this improvement.

The consumption of sugar in Egypt, which was 160,000 metric tons per year at the time of my visit in 1930, has since decreased to 135,000 tons; the production, which was only about 100,000 tons three years ago has now, as a result of favorable government legislation, been increased to 150,000 tons per year, which slightly exceeds the present consumption. This increase in production was easily accomplished by the different plantations making the necessary extension in the areas of land for growing sugar cane. Inasmuch as the sugar industry of Egypt has now succeeded in bringing its production up to the demands of local consumption, which was the main object of the protective policy recently inaugurated by the Egyptian Government, a further expansion of the cane sugar industry of Egypt is not likely to occur under present economic conditions.

In concluding these sketchy personal observations upon the sugar industry in different countries I wish to mention the great cordiality which was extended to me in every country where I made my visitations. It would be impossible to mention the names of all of those to whom I owe obligations. I can only say that as I pursued my journey, which was without a single unpleasant incident, I came to feel more and more that the sugar chemists and sugar technologists of the world constitute a great brotherhood whose chief tenet is the simple requirement of comradeship, helpfulness, and good will.

LITERATURE CITED

(1) Anonymous, *Arch. Suikerind.*, 32, 459–60 (1924).
(2) *Ibid.*, 35, 538–42 (1927).
(3) Ganswijk, C. C. W. van, *Ibid.*, 32, 1065–8 (1924).
(4) Harreveld, P. van, *Ibid.*, 32, 1095–6 (1924).
(5) Inst. for Research in Agr. Eng., *Bull.* 4, Clarendon Press, Oxford, England, 1929.
(6) Kaufman, H. J., *Arch. Suikerind.*, 32, 359–67 (1924).
(7) Krüger, W., "Das Zuckerrohr und seine Kultur," Magdeburg, 1899.
(8) Krüger, W., and collaborators, "Ernährungsverhältnisse, Anbau, Düngung und Krankheiten der Zuckerrübe," Bernburg, 1927.
(9) Rodziewicz, A., *Gaz. Cukrownicza*, 68, 133–5; *Listy Cukrovar.*, 49, No. 26, Rozhledy 24 (1931).
(10) Saillard, E., *La. Planter*, 78, 469–71 (1927).
(11) Schott, G. J., and Harreveld, P. van, *Arch. Suikerind.*, 32; *Mededeel. Proefstation Java-Suikerind.*, No. 14, 449–63 (1924).
(12) Seitz, G. E. G. von, *Arch. Suikerind.*, 28, 519–33 (1920).

RECEIVED April 6, 1932. Presented before the Division of Sugar Chemistry at the 83rd Meeting of the American Chemical Society, New Orleans, La., March 28 to April 1, 1932.

Gel Formation in Sodium Metasilicate Solutions

M. J. PRUCHA AND C. A. GETZ, College of Agriculture, University of Illinois, Urbana, Ill.

SODIUM HYDROXIDE, trisodium phosphate, sodium carbonate, and sodium bicarbonate, used singly or mixed in varying proportions, have been the principal ingredients of the alkaline detergents used in dairy plants for cleaning purposes. Recently another compound has been added to this list of detergents—namely, sodium metasilicate. This compound is especially recommended for the washing of milk bottles in the soaker-type bottle washer.

According to Vail (*1*), sodium metasilicate is an excellent detergent, and in some respects is superior to the other detergents commonly used. However, an objection has been raised against its use in the soaker-type bottle washer on the ground that the washing solutions may form a gel.

The knowledge as regards gel formation in silicate solutions is fully summarized by Vail (*2*). Nevertheless, it seemed desirable to undertake a study to determine what factors may cause gel formation in sodium metasilicate washing solutions when used in dairy operations.

The practice as regards the use and care of the washing solutions in the bottle washers varies in different milk plants. In some cases a fresh solution is prepared daily, whereas in other plants the same solution is used day after day for a month or longer. The strength of the washing solution is maintained by occasional additions of the detergent. Under such practices there will gradually accumulate in the washing solution a considerable amount of milk solids and of acid (mostly lactic) from the milk that adheres to the walls of the bottles.

Another common practice in some plants is to prepare washing solutions by mixing two or more of the different washing powders in varying proportions for the purpose of improving the cleansing properties of the solutions.

In view of these varied practices, the following factors and combinations of them were studied as to their influence on gel formation in sodium metasilicate solutions:

Addition of lactic acid
Addition of other alkaline washing powders
Addition of sour milk and sweet skim milk
Gel formation in other alkaline washing solutions in presence of milk
Addition of other alkaline washing powder, sour milk, and milk solids
Effect of agitation
Effect of temperature

The experiments were carried out in the laboratory as follows: Pyrex glass flasks were used for the solutions. To varying concentrations of sodium metasilicate solutions were added different amounts of lactic acid, sour milk, milk powder, and the different washing powders. Each addition of the above substances was followed by a vigorous shaking. The solutions were allowed to stand for a certain number of hours and then observations as to gel formation were recorded.

The sodium metasilicate used had the composition $Na_2SiO_3 \cdot 5H_2O$.

The results of the experiments are summarized in Tables I to X. The following characters were used in the tables to designate the condition of the solutions studied as regards gel formation:

− denotes no gel formation
± denotes a tendency to gel
+ denotes a weak gel
++ denotes a strong gel

EFFECT OF LACTIC ACID ON GEL FORMATION IN SODIUM METASILICATE SOLUTIONS

In this experiment, the results of which are given in Table I, varying amounts of lactic acid were mixed with sodium meta-

Table I. Effect of Lactic Acid on Gel Formation in Sodium Metasilicate Solutions

Lactic Acid	Percentage Concentration of Sodium Metasilicate																			
%	0.5	1	1.5	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
0	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
2	−	−	−	+	+	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
3	−	−	−	−	++	++	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
4	−	−	−	−	++	++	++	±	−	−	−	−	−	−	−	−	−	−	−	−	−	−
5	−	−	−	−	−	++	++	++	±	−	−	−	−	−	−	−	−	−	−	−	−	−
6	−	−	−	−	−	+	++	++	++	±	−	−	−	−	−	−	−	−	−	−	−	−
7	−	−	−	−	−	−	++	++	++	++	±	−	−	−	−	−	−	−	−	−	−	−
8	−	−	−	−	−	−	+	++	++	++	++	++	+	−	−	−	−	−	−	−	−	−
9	−	−	−	−	−	−	±	++	++	++	++	++	±	−	−	−	−	−	−	−	−	−
10	−	−	−	−	−	−	−	+	++	++	++	++	+	±	±	−	−	−	−	−	−	−

silicate solutions ranging in strength from 0.5 to 20 per cent. The amounts of acid used ranged from 1 to 10 per cent of 75 per cent strength acid. Lactic acid was used because it gets into the washing solutions from the dairy utensils and equipment during the washing operations. The solutions, after being mixed, were allowed to stand at room temperature for 24 hours before observations were recorded.

It will be observed from Table I that no gel was formed in solutions that were strongly acid, even though they contained more than 2 per cent of sodium metasilicate. No gel was formed in solutions that were strongly alkaline, even after the addition of as much as 10 per cent of the acid.

Good gel was formed in those solutions which were near neutral point in reaction. As the acidity of the solution was increased, the gel formation became slower, and the gel formed became weaker. When a certain point in reaction was reached, gel formation ceased.

In a similar manner, as the alkalinity in the solution was increased, starting from the neutral point, the formation of gel became slower and the gel became weaker. When a certain point in alkalinity was reached, gel formation ceased.

The solutions which were outside the gel-forming zone on the acid side were clear; those on the alkali side had a slight precipitate which was due apparently to the hardness of the water used. In the solutions to which 7 per cent or more of lactic acid was added and which were outside the gel-forming zone on the alkaline side, a copious white crystalline precipitate was formed.

Effect of Other Alkaline Washing Powders on Gel Formation in Sodium Metasilicate Solutions

In this experiment sodium hydroxide, trisodium phosphate, sodium carbonate, and sodium bicarbonate were mixed in varying proportions with sodium metasilicate solutions. These were allowed to stand 24 hours before observations were recorded. Table II shows that the addition of sodium hydroxide, trisodium phosphate, or sodium carbonate did not cause gel formation in sodium metasilicate solutions. The addition of sodium bicarbonate, on the other hand, caused gel formation in sodium metasilicate solutions that received 4 per cent or more of the bicarbonate. No gel was formed in the solutions that received less than 4 per cent of the bicarbonate.

Effect of Sour Milk and Milk Solids on Gel Formation in Sodium Metasilicate Solutions

During the washing operations of milk bottles, a considerable amount of sour milk and milk solids may accumulate in the washing solution. The amount will depend on the number of dirty bottles washed and on the length of time the washing solution is used. In Table III are represented the results from an experiment in which varying amounts of sour milk (from 5 to 100 per cent) were mixed with sodium metasilicate solutions of different concentrations. The mixtures were allowed to stand for about 24 hours at room temperature before observations on gel formation were made.

Table II. Effect of Alkalies on Gel Formation in Sodium Metasilicate Solutions

Alkali Added	Percentage Concentration of Sodium Metasilicate						
%	0.5	1	1.5	2	3	4	5
				sodium hydroxide			
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	−	−	−	−	−
3	−	−	−	−	−	−	−
4	−	−	−	−	−	−	−
5	−	−	−	−	−	−	−
				trisodium phosphate			
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	−	−	−	−	−
3	−	−	−	−	−	−	−
4	−	−	−	−	−	−	−
5	−	−	−	−	−	−	−
				sodium carbonate			
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	−	−	−	−	−
3	−	−	−	−	−	−	−
4	−	−	−	−	−	−	−
5	−	−	−	−	−	−	−
				sodium bicarbonate			
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	−	−	−	−	−
3	−	−	−	−	−	−	−
4	−	±	++	++	++	+	−
5	±	±	±	±	±	±	+

Table III. Effect of Sour Milk on Gel Formation in Sodium Metasilicate Solutions

Sour Milk	Percentage Concentration of Sodium Metasilicate						
%	0.5	1	1.5	2	3	4	5
0	−	−	−	−	−	−	−
5	−	−	−	−	−	−	−
10	−	−	−	−	−	−	−
20	−	−	−	−	−	−	−
30	−	−	−	−	−	−	−
50	−	−	±	±	±	±	±
75	−	−	±	±	±	±	±
100	−	−	±	+	+	±	±

In Table IV are presented the results from a similar experiment in which sweet skim milk was used in place of sour milk.

Table IV. Effect of Sweet Skim Milk on Gel Formation in Sodium Metasilicate Solutions

Sweet Milk	Percentage Concentration of Sodium Metasilicate						
%	0.5	1	1.5	2	3	4	5
0	−	−	−	−	−	−	−
5	−	−	−	−	−	−	−
10	−	−	−	−	−	−	−
20	−	−	−	−	−	−	−
30	−	+	±	±	±	±	±
50	−	+	+	±	±	±	±
75	−	++	++	++	+	±	±
100	−	++	++	++	+	+	+

In another experiment, the results of which are given in Table V, all the solutions received 30 per cent of sour milk and varying amounts of milk solids in the form of skim milk powder.

The sour milk used had an acidity of 0.7 per cent of lactic acid. Thirty per cent of such sour milk contributed to the solutions roughly about 2.8 per cent of milk solids and 0.25 per cent of lactic acid.

Examination of Table III shows that gel was formed in 2 and 3 per cent solutions of metasilicate which contained 100 per cent of sour milk. A tendency for gel formation was noticed in 1.5 to 5 per cent solutions containing 50 and 75 per cent of sour milk. (It was difficult to give an exact picture of the condition of the solutions, as regards gel formation, in a tabular form by the use of plus and minus signs.)

When sweet skim milk was used in place of sour milk, a better gel formation took place, as seen in Table IV. A gel was formed in 1 per cent metasilicate solution containing 30 per cent milk, and in 1 and 1.5 per cent metasilicate solutions containing 50 per cent milk. A good gel was formed in 1, 1.5, and 2 per cent metasilicate solutions containing 75 and 100 per cent milk. As the concentration of metasilicate was increased, the gels became weaker and the gelatinous matter tended to break up and settle to the bottom.

No attempt was made to determine why better gel formation took place when sweet skim milk was used than when sour milk was used. Apparently the condition of the milk proteins played a part.

Gel formation also took place in the solutions containing 30 per cent sour milk and 2 and 3 per cent milk powder, as seen in Table V.

TABLE V. EFFECTS OF 30 PER CENT SOUR MILK PLUS VARYING AMOUNTS OF MILK POWDER ON GEL FORMATION IN SODIUM METASILICATE SOLUTION

MILK POWDER	PERCENTAGE CONCENTRATION OF SODIUM METASILICATE 0.5	1	1.5	2	3	4	5
%							
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	±	+	−	−	−
3	−	+	+	+	±	±	±

GEL FORMATION IN SODIUM HYDROXIDE AND TRISODIUM PHOSPHATE SOLUTIONS IN PRESENCE OF MILK

In this experiment sweet skim milk was mixed in varying proportions with solutions of the above alkalies. Observations were made 24 hours later.

It is a well-known fact that, when milk is mixed with solutions of alkaline washing powders, a gelatinous matter may be formed, owing apparently to the reaction between the alkali and the milk proteins.

Table VI shows that a gelatinous precipitate was formed in sodium hydroxide solution when 50 per cent or more of milk was added. In trisodium phosphate solutions a somewhat better gel formation took place.

TABLE VI. EFFECT OF SWEET SKIM MILK ON GEL FORMATION IN SODIUM HYDROXIDE AND TRISODIUM PHOSPHATE SOLUTIONS

MILK	PERCENTAGE CONCENTRATIONS OF ALKALI 0.5	1	1.5	2	3	4	5
%							
				SODIUM HYDROXIDE			
0	−	−	−	−	−	−	−
5	−	−	−	−	−	−	−
10	−	−	−	−	−	−	−
20	−	−	−	−	−	−	−
30	−	−	−	−	−	−	−
50	−	−	−	−	−	−	±
75	−	−	−	±	±	±	±
100	−	±	±	±	±	±	±
				TRISODIUM PHOSPHATE			
0	−	−	−	−	−	−	−
5	−	−	−	−	−	−	−
10	−	−	−	−	−	−	−
20	−	−	−	−	−	−	−
30	−	−	−	−	±	±	±
50	−	−	−	−	±	±	±
75	−	−	−	±	±	±	±
100	−	−	−	±	±	±	±

In sodium metasilicate solutions (Table IV) a tendency to gel formation was noticed in solutions having only 20 per cent of milk, and good gels were formed in the solutions having a higher percentage of milk. From these results it is seen that there is a tendency for gel formation in the solution of all three alkalies, but that in the sodium metasilicate solutions the tendency is much more pronounced. Good gel was formed especially in 1, 1.5, 2, and 3 per cent solutions that received 30 per cent or more of the milk. As the concentration of the metasilicate increased, the gel tended to change into a gelatinous precipitate. In solutions of less than one per cent of metasilicate, no gels were formed.

Another experiment on this point was set up in which solutions of sodium hydroxide, trisodium phosphate, and sodium metasilicate were prepared, having the same sodium oxide content. To each of these solutions were added 30 per cent of sour milk and 3 per cent of milk powder.

The results which are given in Table VII show that no gel formation took place in the solutions of sodium hydroxide and of trisodium phosphate. Good gels were formed in metasilicate solutions which contained 0.29, 0.435, and 0.58 per cent of sodium oxide. In the solutions containing only 0.145 per cent of sodium oxide, no gel was formed; in the solutions containing more than 0.58 per cent of sodium oxide, the gel tended to break up into a gelatinous precipitate.

TABLE VII. GEL FORMATION IN SOLUTIONS OF DIFFERENT ALKALIES[a]

ALKALIES	PERCENTAGE CONCENTRATION OF Na_2O IN SOLUTION 0.145	0.29	0.435	0.58	0.87	1.16	1.45
NaOH	−	−	−	−	−	−	−
$Na_3PO_4 \cdot 12H_2O$	−	−	−	−	−	−	−
$Na_2SiO_3 \cdot 5H_2O$	−	+	+	+	±	±	±

[a] These solutions contained 30 per cent sour milk and 3 per cent milk powder.

The results in Table VII again bring out the fact that gels are formed more readily in sodium metasilicate solutions than in the other alkaline washing-powder solutions in the presence of milk solids.

Gel formation in sodium metasilicate solutions containing milk solids appears to be due to two separate factors: (1) to the reaction between the alkali and the milk solids, as is the case with the solutions of other alkali washing powders; (2) to the gel-forming property of the metasilicate solution itself, which property is not present in the solutions of other alkaline washing powders.

GEL FORMATION IN SODIUM METASILICATE SOLUTIONS IN PRESENCE OF OTHER ALKALI WASHING POWDERS, SOUR MILK, AND MILK SOLIDS

All the solutions in Table VIII received 30 per cent of sour milk. This amount of sour milk was considered as the maximum amount that could accumulate in the washing solutions under the most neglected operations. This amount did not cause gel formation in the metasilicate solutions. The solutions also received 1, 2, and 3 per cent of milk powder.

The addition of sodium hydroxide, trisodium phosphate, or sodium carbonate to sodium metasilicate solutions containing sour milk and milk powder did not seem to increase the tendency of the solutions to form gels.

The addition of sodium bicarbonate caused good gel formation. Comparing Tables VIII and II, it will be noticed that, when no milk solids or sour milk were present in the metasilicate solution, it required 4 per cent of the sodium bicarbonate for gel formation. On the other hand, a gel was formed in metasilicate solutions containing only 0.5 per cent sodium bicarbonate when the solution also contained 30 per cent of sour milk and 2 per cent of milk powder. This again brings out the point that milk solids increase the tendency in metasilicate solutions to gel formation.

The effect of hydrogen-ion concentration on gel formation in general is well known. A thorough study of this phase is reserved for future study. The few determinations already made show that the milk solids lower the hydrogen-ion concentration of the metasilicate solution. A metasilicate solution containing one per cent of milk powder had a pH of 11.9 Two per cent of milk powder lowered the pH to 11.2.

TABLE VIII. EFFECT OF OTHER WASHING POWDERS ON GEL FORMATION IN SODIUM METASILICATE SOLUTION CONTAINING 30 PER CENT OF SOUR MILK AND VARYING AMOUNTS OF MILK POWDER

Milk Powder %	Percentage Concentration of Sodium Metasilicate						
	0.5	1	1.5	2	3	4	5
NO ALKALI ADDED							
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	−	−	−	−	−
3	±	+	+	+	+	+	±
0.5 PER CENT SODIUM HYDROXIDE ADDED							
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	±	±	±	−	−
3	−	±	+	+	±	±	±
1 PER CENT SODIUM HYDROXIDE ADDED							
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	±	±	−	−	−
3	−	±	+	+	±	±	−
2 PER CENT SODIUM HYDROXIDE ADDED							
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	±	±	±	−	−
3	−	−	±	±	±	−	−
1 PER CENT TRISODIUM PHOSPHATE ADDED							
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	±	±	±	±	−	−
3	−	+	+	+	+	±	−
2 PER CENT TRISODIUM PHOSPHATE ADDED							
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	−	−	±	−	−
3	−	+	+	±	±	±	−
1 PER CENT SODIUM CARBONATE ADDED							
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	−	−	−	−	−
3	−	−	−	−	−	−	−
2 PER CENT SODIUM CARBONATE ADDED							
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	−	−	−	−	−
3	−	−	−	±	−	−	−
0.5 PER CENT SODIUM BICARBONATE ADDED							
0	−	−	−	−	−	−	−
0.5	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	±	+	+	+	+
3	−	−	++	++	+	+	+
1 PER CENT SODIUM BICARBONATE ADDED							
0	−	−	−	−	−	−	−
0.5	−	−	−	+	+	−	−
1	−	−	−	+	+	±	−
2	−	−	+	++	+	+	+
3	−	−	++	++	++	++	++
2 PER CENT SODIUM CARBONATE ADDED							
0	−	−	±	+	++	++	+
0.5	−	−	+	+	++	++	+
1	−	−	+	++	++	++	+
2	−	−	+	++	++	++	++
3	−	−	+	++	++	++	++

EFFECT OF AGITATION ON GEL FORMATION IN SODIUM METASILICATE WASHING SOLUTIONS CONTAINING MILK SOLIDS AND LACTIC ACID

During the washing operations of the milk bottles in the bottle-washing machine, the washing solution is violently agitated. When the same solution is used for a number of days, there will gradually accumulate a considerable amount of milk solids and lactic acid from the dirty bottles. Furthermore, when the washing solution is used as stated above, it is necessary to maintain its strength by occasional additions of the washing powder.

This experiment, as reported in Table IX, was an attempt to duplicate such commercial dairy plant practices and was carried out in the following manner:

> In all, eight sets of solutions were prepared. Each set consisted of seven solutions containing, respectively, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, and 5.0 per cent of sodium metasilicate. To each solution was then added a certain amount of milk solids in the form of skim milk powder. The amounts of milk powder used were 0.1, 2, 3, 4, 5, 7, and 10 per cent.
>
> After the milk powder was dissolved, the solutions were treated as follows: A few drops of lactic acid were added and the solution was vigorously shaken. Then a certain amount of metasilicate was added to neutralize the acid. After vigorous shaking, the solution was allowed to stand 10 minutes, and any tendency for gel formation was observed. This procedure was repeated with each solution until the amount of acid as shown in Table VI was used up. After all the acid was added and this in turn neutralized by additions of sodium metasilicate, the final alkalinity of each solution was approximately the same as that at the beginning before any acid was added. The sodium oxide content of the solutions was larger at the end than at the beginning of the experiment:

TABLE IX. EFFECT OF AGITATION ON GEL FORMATION IN SODIUM METASILICATE SOLUTIONS CONTAINING LACTIC ACID AND MILK POWDER

Acid %	Alkalinity Maintained Equivalent to These Percentages of Sodium Metasilicate:						
	0.5	1	1.5	2	3	4	5
NO MILK POWDER ADDED							
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	−	−	−	−	−
3	−	−	−	−	−	−	−
4	+	−	−	−	−	−	−
1.0 PER CENT MILK POWDER ADDED							
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	−	−	−	−	−
3	±	+	−	−	−	−	−
4	±	+	±	−	−	−	−
2 PER CENT MILK POWDER ADDED							
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	−	−	−	−	−
3	±	−	−	−	−	−	−
4	±	+	+	++	±	−	−
3 PER CENT MILK POWDER ADDED							
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	−	−	−	−	−
3	±	−	−	−	−	−	−
4	+	±	±	+	−	−	−
4 PER CENT MILK POWDER ADDED							
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	−	−	−	−	−
3	−	−	−	−	−	−	−
4	+	+	++	++	±	±	±
5 PER CENT MILK POWDER ADDED							
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	−	−	−	−	−	−	−
3	±	−	−	−	−	−	−
4	+	+	++	++	±	−	−
7 PER CENT MILK POWDER ADDED							
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	±	−	−	−	−	−	−
3	±	±	+	±	±	−	−
4	±	+	++	++	+	±	±
10 PER CENT MILK POWDER ADDED							
0	−	−	−	−	−	−	−
1	−	−	−	−	−	−	−
2	±	−	−	−	−	±	±
3	±	+	++	+	±	±	±
4	+	+	++	+	±	±	±

It was observed in this experiment that, when the solutions which would form a gel (if not disturbed) were shaken intermittently, the gel would be broken up to form a gelatinous precipitate. The outstanding point of interest in this experiment from the commercial standpoint is the fact that a large amount of milk solids and of lactic acid was necessary for gel formation.

EFFECT OF TEMPERATURE ON GEL FORMATION IN SODIUM METASILICATE SOLUTIONS

The washing solutions in the bottle washer are usually heated to certain temperatures at which better washing and sterilizing of the bottles is supposed to be obtained. This experiment was carried out to determine the effect of different temperatures on gel formation in the solutions of metasilicate. For this purpose a mixture was selected from Table X which formed a gel at 120° F. (48.9° C.) but which was near the border line. The solution contained the following ingredients: 2 per cent of sodium metasilicate; 1 per cent of sodium bicarbonate; 1 per cent of milk powder; and 30 per cent of sour milk.

TABLE X. EFFECT OF TEMPERATURE ON GEL FORMATION IN 2 PER CENT SOLUTION OF SODIUM METASILICATE

SUBSTANCES ADDED TO SOLN.	TEMPERATURE, ° F.						
	32	50	70	100	120	140	160
1% $NaHCO_3$ 1% milk powder 30% sour milk	–	–	–	+	++	+	+

The solutions were placed at temperatures of 32°, 50°, 70°, 100°, 120°, 140°, and 160° F. (0°, 10°, 21.1°, 37.8°, 48.9°, 60°, and 71.1° C.) and allowed to stay there 24 hours. The solutions kept at 32°, 50°, and 70° F. did not form gels; the solutions at 100°, 140°, and 160° F. formed weak gels; and the solutions at 120° F. formed strong gels.

CONCLUSIONS

1. Sodium metasilicate solutions do not form gel when no other substance is added.
2. The addition of lactic acid causes gel formation in those solutions which are near neutral point in reaction. The gels become weaker as the acidity or the alkalinity of the solution is increased. Gel formation ceases when a certain point in reaction is reached.
3. The addition of other alkaline washing powders, except that of sodium bicarbonate, does not increase the tendency for gel formation.
4. The addition of sodium bicarbonate causes gel formation.
5. The addition of sour milk and milk solids causes gel formation. The milk solids, as well as the acid, lowers the pH value of the solutions.
6. Agitation tends to break up the gel and thus prevent gel formation to some extent.
7. Temperature of about 120° F. (48.9° C.) causes better gel formation than other temperatures.
8. A certain minimum amount of metasilicate is necessary for gel formation. Best gels are formed in solutions containing 1 to 3 per cent of metasilicate. In solutions having higher percentages of metasilicate, the tendency is for the gel to become a gelatinous precipitate.
9. The amount of sour milk and of milk solids necessary for gel formation is large. It requires at least 50 per cent of skim milk before a firm gel is formed. A washing solution containing that amount of milk solids, since its reaction is in the gel-forming zone, will have poor cleansing properties. Gel formation in washing solutions may well be considered as a sign of faulty operations.
10. Apparently gel formation in sodium metasilicate washing solutions in the milk bottle washing machines may take place when the solutions contain less than 3 per cent of the metasilicate and when about 4 per cent or more of the milk solids accumulate.

Hence, gel formation can be avoided by using solutions that contain not less than 3 per cent of the metasilicate and by discarding the washing solutions before about 4 per cent of milk solids other than fat accumulate in them.

LITERATURE CITED

(1) Vail, J. G., Paper presented at meeting of Am. Inst. Chem. Eng., New Orleans, La., Dec. 8–10, 1930.
(2) Vail, J. G., "Soluble Silicates in Industry," A. C. S. Monograph Series No. 46, Chemical Catalog, 1928.

RECEIVED December 11, 1931.

Tests of Chemical Treatments for Control of Sap Stain and Mold in Southern Lumber

R. M. LINDGREN, T. C. SCHEFFER, AND A. D. CHAPMAN

Bureau of Plant Industry, United States Department of Agriculture, New Orleans, La.

DURING the seasoning process at the mill the freshly sawed sapwood of a number of commercially important species of southern woods is subject to permanent discoloration by certain fungi, principally *Ceratostomella* species and some of the *Fungi imperfecti*. Such discolorations have been commonly called blue stains or sap stains because of the color of the portion of the wood attacked. The stain occurs in spots, streaks, or patches of various intensities of color and is due to the dark fungal hyphae which may ramify throughout the sapwood. In addition to stains the fructifications of a number of mold fungi cause discolorations of various hues which are largely superficial in nature and therefore removed in surfacing the wood.

The widespread occurrence of these discoloring fungi has been the source of serious annual losses to pine and hardwood lumber manufacturers, especially in the southern region where the climatic conditions are particularly favorable for their development. Such losses are due principally to reductions in grade, value, and marketability of the stained material. Although the stain and mold fungi do not impair the strength of wood seriously, it is evident that their occurrence injures lumber for uses where a natural finish is desired. Recently buyers have come to discriminate against stained material even in the common grades of lumber.

For some thirty years spasmodic efforts have been made to find an economical means of controlling these fungi in lumber, but not until recently has intensive work been directed at the problem. Because of its economic importance, this problem was selected in 1928 by the Division of Forest Pathology for concentrated effort. As a result of an extensive survey of existing conditions and mill practices in the southern region, it was evident that of the two general methods in use for preventing stain—namely, the use of chemical dipping treatments or of rapid seasoning practices such as kiln drying, end racking, and steaming—the former would lend itself more readily to improvement. The soda dipping treatment, which was being used by some southern mills to control sap stain, had never proved fully satisfactory on pine and had failed completely on hardwoods. It was felt that tests of a sufficient number of chemicals would reveal some of greater efficiency and of wider application than past treatments and therefore of immediate practical value to both pine and hardwood manufacturers. The present paper summarizes the results of a number of such tests conducted over the 3-year period 1929 to 1931.

SMALL-SCALE TESTS

Since it was obviously impossible to make tests on a commercial scale of all the chemicals warranting trial, prelimi-

TABLE I. RELATIVE EFFECTIVENESS OF CHEMICALS USED IN PRELIMINARY EXPERIMENTS ON CONTROL OF SAP STAIN AND MOLD IN PINE AND SAP GUM[a]

CHEMICALS TESTED[b]	CONCN.[c]	PINE			SAP GUM	
		Tests	Av. of sapwood stained	Av. of sapwood molded	Tests	Av. of sapwood stained
	%		%	%		%
$Al_2(SO_4)_3$	7.2	3	24	5	3	37
$Al_2(SO_4)_3K_2SO_4$	7.1	3	40	4	3	39
Ammonium borate	1.2	2	65	0.8	3	12
Ammonium borate	1.6	1	63	9	1	58
NH_4F	1.08	3	5	62	1	46
NH_4F	1.5	3	10	45	3	40
NH_4F + sodium *o*-phenylphenoxide	0.5, 0.5	1	7	30	1	5
NH_4F + sodium *o*-phenylphenoxide	1.3, 0.4	1	4	18	1	10
NH_4F + sodium *o*-phenylphenoxide	0.5, 0.4	1	8	1.5	1	13
As_2O_3 (10% soln.)	2.4	2	25	45	1	27
$BaCO_3$	6.0	2	19	10	2	73
$Ba(OH)_2$	6.0	2	34	0.1	2	31
$BaSO_4$	2.4	2	36	4	2	51
Benzoic acid	0.9	3	61	31	3	47
β-Naphthol + naphthalene + NaOH	0.56, 0.40, 0.16	3	18	6	1	53
Borax	7.7	3	6	17	1	5
Borax	7.2	4	13	14	4	2
Borax	5.4	5	37	5	6	2
Borax	7.2	1	15	..	.	..
Borax + NaOH	5.4, 0.3	3	61	5	4	4
Borax + NH_4OH + NaOH	5.4, 0.6, 0.3	2	43	14	2	6
Borax + sodium *o*-phenylphenoxide	4.2, 0.3	3	37	2	3	4
Bordeaux	1.2	2	48	0	2	46
Boric acid	3.6	3	33	45	1	7
Boric acid + $ZnSO_4$	1.8, 1.8	3	57	5	4	9
$CdSO_4$	0.3	3	16	9	1	56
Colloidal creosote	0.9	1	83	Trace	2	76
Cu_2CO_3	1.2	3	54	1	4	53
Cu_2CO_3 + borax	0.3, 5.4	.	..	..	1	1
Copper phenylsulfonate	0.45	3	79	Trace	4	61
$CuSO_4$	3.6	1	12	0	2	13
$CuSO_4$	1.2	1	48	7	1	25
$CuSO_4$ + NH_4OH	3.0, 0.6	2	13	1	3	22
Cresylic acid (crude 97–99%) + NaOH	1.9, 0.8	3	22	4	1	50
Dipdust	0.48	1	59	0	1	87
Diversol	2.4	2	58	1	2	63
Ethyl chloroacetate	0.21	.	..	..	1	69
Ethylmercury chloride, 3 parts; inerts, 97 parts (No. 652)	0.24	3	2	2	3	1
Ethylmercury chloride, 3 parts; inerts, 97 parts (No. 652)	0.48	3	0.6	12	3	0.5
Ethylmercury chloride, 4.3 parts; inerts, 95.7 parts (No. 745)	0.48	1	5	41	1	0.7
Ethylmercury chloride, 4.3 parts; inerts, 95.7 parts (Lignasan)	0.48	1	0.1	0	.	..
Ethylmercury chloride, 4.3 parts; inerts, 95.7 parts (No. 745-B)	0.24	4	20	7	5	3
Ethylmercury chloride, 3 parts; Wyandotte soda, 97 parts (K-1)	0.57	3	3	5	1	4
Ethylmercury chloride (K-1) + additional soda	0.3, 5.3	2	5	6	.	..
Ethylmercury cyanide, 2 parts; inerts, 98 parts (No. 697)	0.48	1	22	13	1	46
Ethylmercury fluoride, 2 parts; inerts, 98 parts (No. 696)	0.48	1	4.8	82	1	0.3
Ethylmercury oxalate, 3 parts; inerts, 97 parts (No. 674)	0.48	3	0.2	8	3	0.7
Ethylmercury phosphate, 3 parts; inerts, 97 parts (No. 673)	0.48	4	1	15	4	0.6
Ethylmercury phosphate (No. 961)	0.24	1	31	10	2	10
Ethylmercury phosphate, 3 parts; inerts, 97 parts (No. 673)	0.48	1	0.1	0	.	..

(Continued on page 74)

[a] Tests in 1929 were conducted at Great Southern Lumber Company, Bogalusa, La.; Eastman-Gardiner Lumber Company, Laurel, Miss.; and J. J. Newman Lumber Company, Hattiesburg, Miss. Tests in 1930 were conducted at Eastman-Gardiner Lumber Company, Laurel, Miss.; Louisiana Central Lumber Company, Clarks, La.; and W. T. Smith Lumber Company, Chapman, Ala. Tests in 1931 were conducted at Goodyear Lumber Company, Picayune, Miss.; Jasper County Lumber Company, Jasper, Tex.; Gloster Lumber Company, Gloster, Miss.; Eastman-Gardiner Lumber Company, Laurel, Miss.; Tremont Lumber Company, Rochelle, La.; Grant Timber and Manufacturing Company, Selma, La.; and E. L. Bruce Lumber Company, Laurel, Miss.

[b] Bordeaux, powdered form, Orchard brand.
Colloidal creosote, supplied by Baird and McGuire, Inc., Holbrook, Mass.
Dipdust, a patented disinfectant consisting of 6% hydroxymercurichlorophenol sulfide, 2% hydroxymercurinitrophenol sulfate.
Diversol, a patented sterilizing agent composed of 2.5% sodium hypochlorite, 92.5% alkaline sodium phosphate.
Ethylmercury compounds, phenylmercury acetate, sodium silicofluoride (50%), furnished by the E. I. du Pont de Nemours & Company, Wilmington, Del.
Fungimors, a patented German stain preventive understood to be mercurial.
Ialine, a reversible colloidal sulfur.
Mercurophen, a mercury compound (sodium oxymercuri-*o*-nitrophenoxide), furnished by H. K. Mulford Company.
Metaphen, an organic mercury compound (4-diacetoxymercuri-2-nitrocresol).
Minerec, a flotation reagent consisting of 10% xanthic anhydride and 90% ethyloxycarbonyl sulfide, furnished by the Minerec Corporation.
Nekyan, a patented Swedish stain preventive.
Pine oil emulsion, a steam-distilled emulsified pine oil, furnished by the Johnston-Mackie Company.
Protexwood, a product of the destructive distillation of wood, furnished by the Termiteol Corporation of Louisiana.
Semesan, a patented disinfectant (hydroxymercurichlorophenol).
Shirlan compounds, proprietary British antimildew compounds used in conditioning cotton yarn.
Soda (Wyandotte), a mixture of carbonate and bicarbonate, furnished by the J. B. Ford Agency. In the large-scale tests a sodium bicarbonate, manufactured by the Mathieson Alkali Works, was used also.
Sodium *o*-phenylphenoxide, sodium 2-chloro-*o*-phenylphenoxide, tetrachlorophenol, and sodium tetrachlorophenoxide, furnished by the Dow Chemical Company, Midland, Mich.
Solbar, a compound principally of barium sulfide, furnished by E. I. du Pont de Nemours & Company, Wilmington, Del.
Sterilac, an alkaline chloroamine mixture used for disinfectant purposes.
Tri-Treat, a patented wood preservative, furnished by Bruce Chemical Company.

[c] Concentration of all solutions selected on the basis of an approximate cost of solution of 20 cents per thousand board feet of lumber. In the case of mixtures, the concentration per cent is figured on the basis of the weight of the total sample (including inerts) unless the individual concentrations are given in the order of the components named.

nary tests were made on a small scale under actual mill conditions. Such small-scale tests, which are less costly and time consuming than commercial trials, have permitted the testing of a large number of untried chemicals and the elimination of all but the most effective ones. They have proved of value also in determining the influence of concentration and temperature changes on the efficiency of the most promising treatments. The technic employed, permitting as it does the close control of environmental factors, assures uniform conditions of exposure and therefore an accurate comparison of a large number of chemicals at one time. Such a condition is not attainable in commercial testing. The reliability of the method for the intended purposes is indicated by the consistency of the results and the corroborative evidence from subsequent commercial trials of the most promising treatments.

Table I. Relative Effectiveness of Chemicals Used in Preliminary Experiments on Control of Sap Stain and Mold in Pine and Sap Gum[a] *(Continued)*

		Pine			Sap Gum	
Chemicals Tested[b]	Concn.[c]	Tests	Av. of sapwood stained	Av. of sapwood molded	Tests	Av. of sapwood stained
	%		%	%		%
Ethylmercury sulfate, 5 parts; inerts, 95 parts (No. 647)	0.48	3	0.2	10	3	0.4
Ethylmercury tetraborate, 2 parts; inerts, 98 parts (No. 730)	0.48	1	5	27	1	1
$FeSO_4$	7.2	1	6	12	1	18
Formaldehyde	1.2	3	43	36	3	62
Fungimors	0.3	3	17	21	1	63
Ialine	0.24	2	30	3	2	20
Lime sulfur	0.6	2	35	0	2	38
$MgSiF_6$	0.6	3	45	9	3	45
$HgCl_2$	0.16	3	11	20	1	29
HgI_2	0.05	1	33	0	1	8
HgI_2 + KI	0.15, 0.19	3	0.7	3	3	3
HgI_2 + KI + soda	0.028, 0.028, 2.4	2	62	Trace	3	57
Mercuric salicylate	0.11	3	70	Trace	4	59
Mercurophen	0.3	1	35	36	1	43
Metaphen	0.3	2	36	7	2	42
Minerec	0.24	1	57	1	1	53
Minerec	0.32	1	3	0	.	..
Nekyan	2.7	3	31	9	1	46
p-Dichlorobenzene	1.45	3	30	10	1	54
Phenylmercury acetate, 3 parts; inerts, 97 parts (P. M. A.)	0.57	3	7	6	1	8
Phenylmercury nitrate ("X" compound)	0.08	1	3	12	1	2
Phenylmercury nitrate ("X" compound)	0.13	1	0.1	0	.	..
Phenyl salicylate	0.6	1	11	0	2	52
Pine oil emulsion	2.4	2	32	13	1	67
K_2S	3.0	3	18	1	3	41
Protexwood	3.0	1	52	0	1	44
Salicylic acid	1.8	3	28	30	3	42
Semesan	0.48	2	27	10	2	17
Shirlan N. A.	0.5	1	38	0	.	..
Shirlan (50% paste)	0.9	1	32	0	.	..
Shirlan powder	0.2	1	38	0	.	..
Soda (Wyandotte alkali)	7.2	3	4	1	1	43
Soda	7.2	4	3	0.7	4	31
Soda	5.3	3	4	2	3	34
Soda (in use in vat)	11.0	1	6	..	.	..
Soda	5.4	3	63	0.8	4	58
Soda	7.2	1	0.8	0	.	..
Soda + borax	3.6, 3.8	1	7	12	.	..
Soda + $NaHSO_3$	3.8, 2.9	2	20	5	.	..
Soda + NaF	3.5, 1.9	3	7	4	.	..
Sodium benzoate	1.2	3	51	21	3	62
$NaHSO_3$	7.2	3	23	71	1	60
Sodium 2-chloro-*o*-phenylphenoxide	0.4	2	0.4	0.1	2	7
Sodium dinitrophenoxide	1.2	2	3	0	2	39
Sodium dinitrophenoxide	0.9	1	77	0	2	31
Sodium dinitrophenoxide	0.15	1	72	1	1	85
Sodium dinitro-*o*-phenylphenoxide	0.48	3	5	0.5	2	20
NaF	4.1	3	7	27	1	18
NaF + borax	2.08, 3.35	2	21	29	.	..
NaF + $NaHSO_3$	1.9, 3.5	2	14	77	.	..
NaOCl	3.1	2	75	10	2	35
NaOCl	4.2	2	67	7	2	74
Na_2SiO_3	5.4	3	58	0.5	4	47
Na_2SiO_3	6.4	1	1.5	0	.	..
Sodium monoborate	5.4	1	60	0	1	2
Sodium naphthionate	0.21	1	80	Trace	2	69
Sodium *o*-phenylphenoxide	0.9	4	9	2	4	14
Sodium *o*-phenylphenoxide	0.48	3	4	0.1	2	27
Sodium *o*-phenylphenoxide	0.3	1	1.5	0.4	1	14
Sodium *o*-phenylphenoxide	0.9	1	10	0	1	1
Sodium phenylsulfonate	0.9	3	63	3	4	60
Na_3PO_4	6.0	3	33	8	3	35
$Na_2SiO_3.9H_2O$	3.2	3	32	9	1	67
Na_2SiF_6	0.9	2	7	50	2	44
Na_2SiF_6, 50% (No. 733)	1.9	1	42	11	1	67
Na_2SiF_6, 50% (No. 733)	0.9	1	82	0	2	63
Sodium tetrachlorophenoxide	0.48	1	30	0	1	9
Sodium tetrachlorophenoxide	0.48	3	3	0.2	2	0.3
Sodium tetrachlorophenoxide + sodium *o*-phenylphenoxide	0.48, 0.48	2	1.3	0.6	2	0.8
Sodium tetrachlorophenoxide + sodium *o*-phenylphenoxide	0.24, 0.24	1	9.4	0	1	7
Solbar	0.4	2	68	9	2	35
Sterilac	0.15	2	21	7	2	35
Tetrachlorophenoxide + NaOH	1.3, 0.16	3	47	0	4	5
Tri-Treat	3.3	1	52	0	1	36
ZnF_2	3.2	1	80	0	1	58
Zinc phenylsulfonate	0.9	3	75	1.3	4	67
Untreated checks	..	3	52	20	1	71
Untreated checks	..	4	52	9	4	48
Untreated checks	..	6	65	0.5	6	60
Untreated checks	..	3	64	0	3	68

In selecting the chemicals for trial and in evaluating them later for stain control, such qualities as cost, ease of solution and application, effect on equipment and color of lumber, and injuriousness to workmen were considered, as well as toxicity to stain and mold organisms. Included in the group selected was a large number of organic and inorganic salts of the heavy and alkali metals, and chlorinated and nonchlorinated phenol compounds. Some of the materials had shown promise in closely related lines of investigation; others were proprietary compounds recommended as stain preventives in the United States and in foreign countries; the remainder was untried chemicals which had shown promise in laboratory toxicity tests on the sap stain fungi (*1*). Data on the extent to which each of these treatments met the requirements enumerated above were gathered during the course of the tests which continued through the summers of 1929, 1930, and 1931.

The usual procedure in treating was to immerse freshly sawed pieces of sapwood, 1 × 2 × 24 inches (2.5 × 5 × 61 cm.) in size, for 15 seconds in solutions kept at a temperature of 160° F. (71.1° C.). In some of the tests, especially in the later ones, the solutions were also applied at air temperatures to determine the extent to which the application of heat increased the effectiveness of the treatment. The initial concentrations of most of the chemical solutions were based on an approximate cost for materials of 20 cents per thousand board feet of lumber treated, the highest cost considered practicable by most southern operators. The dipped pieces, together with untreated control material for comparison purposes, were semibulk-piled in a moist location which presented uniformly severe moisture conditions for the different treatments. At the end of a testing period of 30 to 40 days, the piles, each of which contained forty to sixty pieces, were examined and the effectiveness of each of the various treatments determined on the basis of the percentage of sapwood stained and molded.

RESULTS OF TREATMENT

The results of the preliminary small-scale tests are presented in Table I. Mold occurrence in gum is not included because of its unimportance in all treatments. Where a treatment was used in two or more trials, an average figure of effectiveness in stain and mold control at the various mills is given. The term "stain," as used here, is meant to include those fungous discolorations, usually bluish black in color, which are not readily removed in surfacing the lumber. The results of the hot and cold treatments were averaged and are presented as one figure because little or no difference in effectiveness was noted, with the exception of those solutions containing sodium carbonate or bicarbonate, in which case the hot treatments were definitely superior to those applied at air temperatures.

The degree of control obtained by any given treatment varied somewhat at different mills as would be expected of tests made in the field under widely varying conditions of humidity and temperature. The results of the tests, however, are fairly consistent, in that the different treatments ranked in about the same order of efficiency in different experiments.

Of the one hundred or more treatments tested, several were quite effective in controlling stain and mold in both pine and hardwoods; others prevented stain but not mold, or vice versa, or were limited in effectiveness to one kind of wood. Borax, for instance, proved effective on hardwoods but relatively ineffective on pine, whereas the reverse condition held true for sodium *o*-phenylphenoxide. Ammonium fluoride controlled stain effectively but permitted too much mold growth to be of practical value unless combined with a compound effective in preventing mold development.

Of the entire list, only the following compounds were believed to combine enough of the required qualities of a practical treatment to warrant commercial trial: borax, ethylmercury chloride, ethylmercury phosphate, sodium *o*-phenylphenoxide, sodium tetrachlorophenoxide, and sodium 2-chloro-*o*-phenylphenoxide. These, with the exception of the last-named compound, have already been tested on a commercial scale—borax on hardwoods only, and the remainder on both pine and hardwoods. The results of these commercial tests, which have been published briefly elsewhere, corroborate closely those reported in the present paper (*2*). Soda, the principal treatment in current use, was included as a standard of comparison in all large-scale trials on pine, and proved definitely inferior to the other treatments tested.

Although most of the treatments used in the preliminary tests were eliminated on the basis of ineffectiveness against stain and mold fungi, several which looked promising from the standpoint of control possessed certain qualities which made them undesirable. For example, mercuric chloride, Fungimors, mercuric iodide plus potassium iodide, and certain of the organic mercury compounds were eliminated because of corrosiveness to metal or possible injuriousness to workmen handling them. Others, such as sodium dinitrophenoxide, copper sulfate alone or in mixture, ferrous sulfate, and Protexwood were objectionable because of their discoloring effect on wood.

Under average drying conditions the critical period for stain occurrence in lumber is during the first 30 days of seasoning. If staining does not occur within that period, the surface moisture content of the lumber has in most cases been reduced sufficiently to prevent further infection by staining organisms. For this reason the tests were run for periods not longer than 40 days and no attempt was made to determine the permanence of the treatments over longer periods of time. It has become evident, however, that a certain degree of permanence is an important quality and one upon which more emphasis must be placed in further tests. Lumber stacks in the South are frequently exposed to heavy rains, which prolong the period of susceptibility to discoloration either by retarding drying of the green lumber or by increasing the moisture content of the dried stock sufficiently to permit stain development. Under such conditions the toxic elements of some of the present treatments may be removed by leaching or volatilization to the extent that their efficiency will be greatly reduced. The only instance in which permanence might not be desirable is in the treatment of stock to be used for food containers, where chemicals with an offensive odor or high toxicity to humans would be undesirable.

SUMMARY

Of the one hundred or more chemicals and combinations of chemicals tested for the control of stain and mold on pine and hardwood lumber, borax, ethylmercury chloride, ethylmercury phosphate, sodium tetrachlorophenoxide, and sodium *o*-phenylphenoxide show greatest promise of commercial practicability. Although at least one of the above treatments has already been adopted in commercial practice, further work is essential before their maximum efficiency under various conditions of application can be assured. The search for new materials as well as experimentation directed at the improvement of the best of the present treatments will be continued.

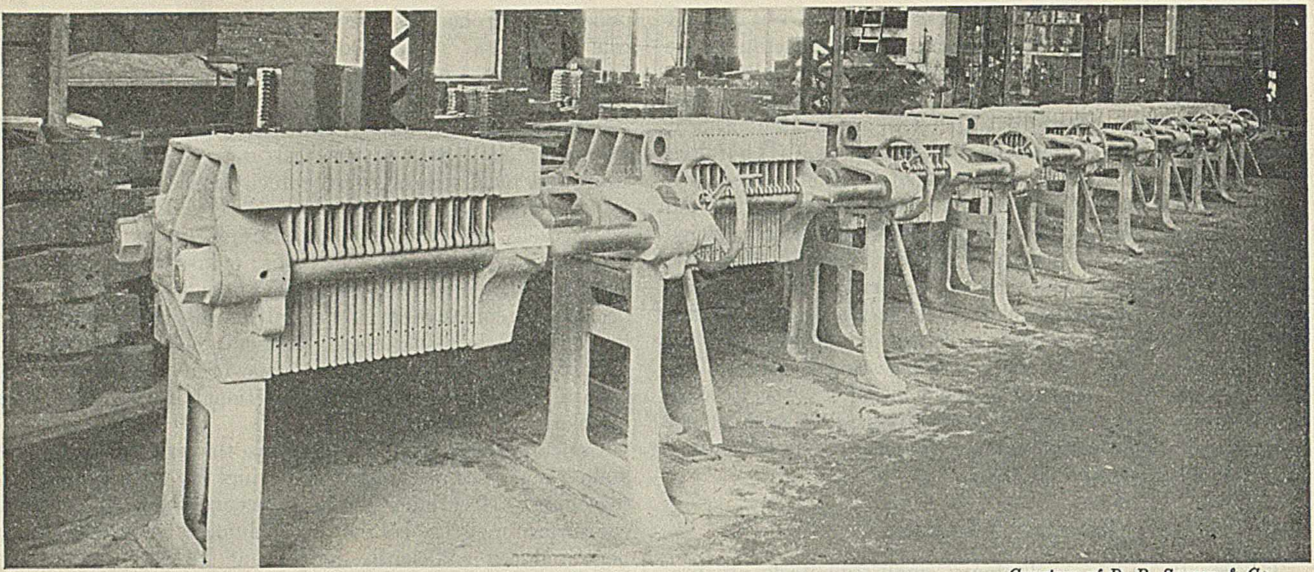
LITERATURE CITED

(1) Hatfield, I., *Proc. Am. Wood-Preservers' Assoc.*, 27, 304–14 (1931); 28, 330–340 (1932).

(2) Lindgren, R. M., Scheffer, T. C., and Chapman, A. D., *Southern Lumberman*, 145, 43–46 (May 15, 1932).

RECEIVED August 4, 1932. The tests were conducted by the Bureau of Plant Industry in coöperation with the Southern Forest Experiment Station and the American Pitch Pine Export Company, New Orleans, La., and its member mills.

♉ ☿ ♆



Courtesy of D. R. Sperry & Co.

RAYON FILTER PRESSES

Studies in Filtration

I. Critical Analysis of Filtration Theory

B. F. RUTH WITH G. H. MONTILLON AND R. E. MONTONNA, University of Minnesota, Minneapolis, Minn.

The derivation of two types of equations governing filtration is reviewed and their failure to express adequately experimental data pointed out. The confusion of results obtained by different investigations is shown. The concept of specific resistance is examined and found to be invalid. It is demonstrated that only for incompressible materials is it possible to derive an equation from theoretical grounds—i. e., from Poiseuille's law. The necessity for a study of the early stages of the filtration cycle for a large variety of substances to establish experimentally the exact relation between resistance and the variables affecting it is shown.

THIS series of papers will present the results of an investigation which has been the outgrowth of an attempt to solve some of the difficulties encountered in the practical determination of filter constants in the laboratory. In 1927 an experiment of this nature was introduced into an undergraduate laboratory course in chemical engineering at the University of Minnesota. Filtration tests were carried out by numerous groups of four or five students, employing suspensions of Filter-Cel in a 12-inch (30.5-cm.) Sperry plate and frame press. The data thus obtained were treated in accordance with the accepted equations appearing in Walker, Lewis, and McAdams' book (*31*) and by means of the analytical methods of Baker (*5*) and of Waterman and van Gilse (*34*), as previously used by Jewett and Montonna (*17*). Although as a rule the results compared favorably with those in the literature, they were often regarded as failures by students. For the first time in their scholastic experience they encountered a physico-chemical phenomenon which at times displayed inexplicably erratic behavior, and in no case exhibited a wholly satisfactory agreement with theory. The explanation that the accuracy of the data might not warrant closer adherence to theory was refuted by special and painstaking repetition of the work by several groups. The conviction became general that perhaps the equations should be modified in some respect. In view of the general dissatisfaction, it was considered advisable to discontinue class experiments until staff research or investigation of the literature could solve the difficulties.

One of the troubles for which it had been found most difficult to render a satisfactory explanation had been the almost universal failure of the tests to agree with the behavior predicted by theory in the early stages of the filtration. Investigation of the literature revealed that this behavior was not peculiar to student tests alone, but that it had been observed by a number of experimenters. While the general consensus of opinion seemed to be that its effect might be neglected in the practical determination of filtration constants for engineering purposes, an interesting and thorough mathematical discussion of the phenomenon had been made recently by Underwood (*27*). Through this paper attention was attracted to the fact that no direct experimental study of the initial stages of a filtration had ever been performed, and that Underwood's analysis had been made only upon such data as were available in the literature. These had been taken primarily in an effort to establish the more general and fundamental relations predicted by theory, rather than as an accurate study of the filtration process per se. Moreover, the apparatus which had been employed did not seem well adapted for the accuracy in observation which is often required in the initial stages of a filtration where rate of filtrate flow is rapid. Those workers who had utilized plant-scale equipment were necessarily handicapped by the difficulty in accurately measuring large volumes of filtrate. On the other hand, those who did not use plant-scale equipment had

Vol. 25.

worked at the other extreme—with suction filters of quite small area, or with small laboratory presses operated by hand pumps.

It was concluded that an investigation of the early stages of a filtration, carried out upon equipment sufficiently large to insure results comparable with commercial practice, yet small enough to permit accurate measurements upon the filtrate volume, was a highly desirable research.

General Filtration Theories

In order to evaluate properly the results of this investigation, it is necessary to present a brief outline of the development and present status of the subject of filtration. Existing filtration equations may be divided into two groups: those appearing in standard chemical engineering texts (*3*, *31*), generally termed the Lewis equations, and the various forms of Sperry's equation as modified by foreign workers. The essential difference between them is the manner in which the effect of filter-base resistance is treated. Because of the fact that Sperry's treatment leads to a more formidable expression, the Lewis equation has been generally accepted for engineering purposes. This equation originated in the work of Almy and Lewis (*2*), who filtered chromium hydroxide in a small plate and frame press at a series of constant pressures. By means of a logarithmic treatment of their data, they secured the equation:

$$\frac{dV}{d\Theta} = 13{,}600\,\frac{P^{27}}{V^{81}}$$

by means of which they were able to correlate their results through a pressure range of 5 to 100 pounds per square inch (0.4 to 7 kg. per sq. cm.). They concluded that the rate of filtrate flow was a power function of both the pressure and the volume of filtrate, and that an equation of the form:

$$\frac{dV}{d\Theta} = \frac{KP^{n}}{V^{m}}$$

constituted the basic law of filtration.

Sperry's equation (*22*, *23*) was deduced from theoretical rather than experimental considerations. These had been prompted by the analogy between the filtration process and the flow of ground water. Since, for the latter, Poiseuille's law had been shown to hold, Sperry postulated that Poiseuille's law was also the basic law of filtration. Upon this theoretical basis he was able to derive a quite general equation in which rate of flow was considered to be strictly proportional to the first power of P and V, and in which provision was also made for the effect of filter-base resistance and variation in filtrate viscosity.

Baker (*5*) employed a similar analogy, but disagreed with Sperry by postulating that the rate of flow was proportional to indefinite powers (n and m) of pressure and volume, in accordance with the earlier conclusions of Almy and Lewis (*2*). Upon this basis he secured an equation of the form:

$$\frac{dV}{d\Theta} = \frac{KA^{2}P^{n}}{V^{m}}$$

for which the integrated expression is

$$V^{(m+1)} = (m + 1)KA^{2}P^{n}\Theta$$

He considered that this derivation furnished a theoretical basis for the earlier empirical equation and utilized it in the treatment of data secured by filtering defecated sugar solutions containing kieselguhr as a filter aid. His method of determining m consisted in plotting V raised to various powers against the filtering time, Θ. That value of (m + 1) which gave, by trial and error, the straightest line was considered the best. His method of determining n required additional filtrations performed at constant rate. His results have been justly criticized by Sperry (*24*), who pointed out that, whereas Baker obtained values of n near 2, the solution for n which is possible by another method from his constant-pressure filtrations upon the same sludge, yields a value of n between 0.7 and 0.8.

A better solution for n was given by Waterman and van Gilse (*34*). According to these workers, if several filtrations performed at different constant pressures are compared at points where equal volumes of filtrate have been collected, the following relations hold:

$$V_1^{(m+1)} = (m + 1)KA^{2}P_1^{n}\Theta_1 \qquad (1)$$

$$V_2^{(m+1)} = (m + 1)KA^{2}P_2^{n}\Theta_2 \qquad (2)$$

When V_1 is taken equal to V_2, the right-hand sides of Equations 1 and 2 may be set equal. Solving for n,

$$n = \frac{\log \Theta_2 - \log \Theta_1}{\log P_1 - \log P_2}$$

In the analysis of filtration data by students, the method of Baker for m and that of Waterman and van Gilse for n were employed. The solution for m was largely a matter of form, since it consisted only in showing for a typical case that, in accordance with the results of Baker, a value of (m + 1) = 2 yielded the straightest line for suspensions of a fairly noncompressible material such as Filter-Cel.

Figure 1 illustrates the typical S-shaped curvature of a $V^2 = \Theta$ plot as secured by Baker, and as observed in hundreds of filtrations performed in these laboratories. Although the relative curvatures may vary in degree from case to case, they are present without exception in every filtration carried out to complete filling of the frame. The downward curvature at the end of the test is easily explained by the fact that the area for filtrate flow begins to decrease after the cakes make contact near the end of the test. The upward curvature at the beginning of the test has been explained in various ways. With the exception of Underwood, the general consensus of opinion seems to be that this failure of the initial stages to fall upon the straight line may be neglected, since the complications of the initial stages of a filtration are of little importance in developing a practical theory (*4a*). Nevertheless, examination in these laboratories of a great many plots similar to Figure 1 has revealed that, although they appear to be straight for the greater part, the truly straight portion often comprises less than 50 per cent of the test. This is due to the contracted scale that results when the square of volume is plotted. The deceptive character of such an analysis is well illustrated in Figure 1 where, although the curvatures are approximately similar, the downward portion at the end of the test comprises less than 5 per cent of the total filtration, compared to 50 per cent for the upward curvature at the start. Whether the true magnitude of this neglected initial stage has been perceived by workers in the past is not apparent. In any case, it would seem that this neglected portion is cosind-

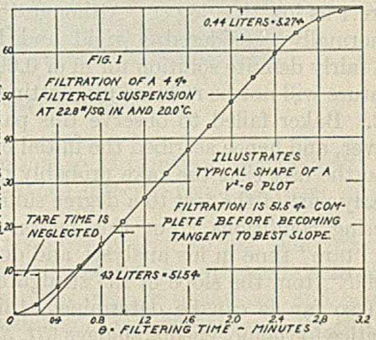


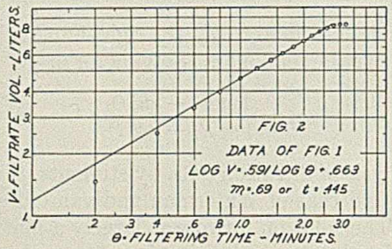
FIG. 1

FILTRATION OF A 4% FILTER-CEL SUSPENSION AT 22.8#/SQ. IN. AND 20.0°C.

ILLUSTRATES TYPICAL SHAPE OF A V²-Θ PLOT erable, and perhaps comprises just as important a part of the filtration period as the latter stages.

Development of Lewis Equations

Baker attempted to straighten such plots by raising V to various powers between 1.8 and 2.2. This was done in an effort to identify the curvature with the m of the Almy and Lewis equation. He found, however, that no assignable value of (m + 1) would reduce the curvature, and, in fact, that the straightest plot resulted when (m + 1) was taken as 2. He consequently concluded that 2 represented the best value of (m + 1) for sludges of such rigid material as kieselguhr. But in view of the results of Almy and Lewis, who secured m = 0.81 for chromium hydroxide, he made the qualification that the probable limit of variation for all materials was between 1.8 and 2.2. It should be pointed out that had he utilized the logarithmic analysis of Almy and Lewis, he would have secured quite definite values of m in the neighborhood of 0.8, notwithstanding the great difference in the nature of the sludges. In Figure 2 this has been illustrated by plotting the data of Figure 1 as log V *vs.* log Θ. Although the material is Filter-Cel (normally considered a rigid and homogeneous substance), a fairly definite solution for m of 0.69 is obtained; yet the curvature will not be reduced by plotting V to powers other than 2. Baker failed to observe this paradoxical behavior, however, and hence ascribed the initial curvature of a $V^2 = \Theta$ plot to the fact that the cake probably does not form during the early part of the test to a degree sufficient to yield uniform filtering conditions. For this reason he neglected the initial or "tare" time in his analysis, and determined the value of $2KA^2P^n$ from the slope of the straightest portion of the plot. In so far as can be determined, this is still the accepted practice for homogeneous sludges (*31, 3*).



Weber and Hershey (*35*) reviewed a number of Massachusetts Institute of Technology theses, giving for the first time the derivation of the equations as presented at an earlier date in "Principles of Chemical Engineering" (*31*), as well as explaining the assumptions upon which they were based. In their treatment the differential rate of filtrate flow during the filtration is given by:

$$\frac{dV}{d\Theta} = \frac{PA^{2+t}}{rP^s\int\left(\frac{dV}{d\Theta}\right)^t d(vV)} = \frac{P^{1-s}A^{2+t}}{r''v\int\left(\frac{dV}{d\Theta}\right)^t dV} \qquad (3)$$

The integration of this equation for the general case is given as:

$$\left(\frac{V}{A}\right)^{2+t} = \frac{P^{1-s}}{r''(1+t)v}\left(\frac{2+t}{1+t}\Theta\right)^{1+t} \qquad (4)$$

The integration of this equation is quite difficult and beyond the ability of the ordinary student. Underwood (*29*) states, moreover, that it contains an error, and submits a somewhat different solution.

In the evolution of the original equation of Almy and Lewis into this form a number of new conceptions have been introduced. m has become replaced by t and is interpreted for the first time as a coefficient of "scouring effect." n has been replaced by $(1 - s)$. The substitution of $(1 - s)$ for n arises through an improvement upon the original theory, whereby a conception of specific resistance is introduced. Thus the average resistance per unit cube of cake is expressed as:

$$r = r''P^s\left(\frac{dV}{d\Theta}\right)^t$$

where r'' = resistance of unit cube when under unit pressure, with unit rate of filtrate flow passing through it.

The conception of specific resistance possesses certain mathematical advantages over the earlier specific permeability of Sperry. In adopting it, however, the earlier hypothesis of Lewis that it is rate of flow which is proportional to a power n or $(1 - s)$ of the pressure has been abandoned. The equation is now brought into conformity with Poiseuille's law and the postulates of Sperry, although the latter had previously been severely criticized (*6*).

It was evidently intended that the exponent $(2 + t)$ should not fulfil the same function as (m + 1) in the earlier equation. This is apparent from the postulate that noticeable scouring effect can occur only in filter cakes composed of a mixture of two precipitates, and especially when a slimy precipitate is mixed with a filter aid. Weber and Hershey have indicated how Equation 4 reduces to the form:

$$\log V = \log K' + \left(\frac{1+t}{2+t}\right)\log\Theta \qquad (5)$$

which enables the value of t to be determined for a heterogeneous sludge by plotting log of volume *vs.* log of time for constant-pressure filtrations.

For homogeneous sludges, which comprise perhaps the most numerous class of commonly filtered materials, scouring effect is negligible, and therefore t should equal zero. For this case the general equation reduces to:

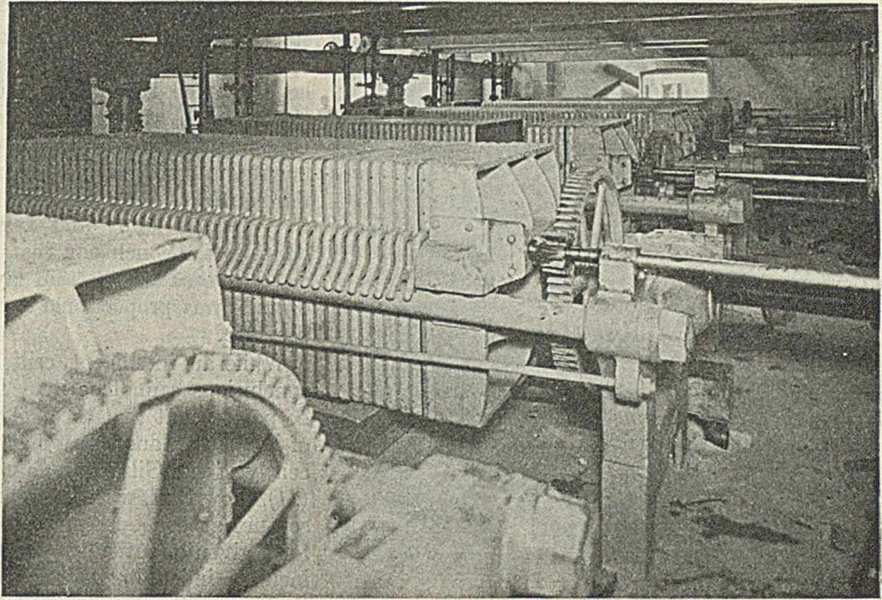
$$V^2 = \frac{2A^2P^{1-s}}{r'v}\Theta$$

In the analysis of such data, it is recommended (*32*) that "V^2 be plotted *vs.* Θ; an error in locating zero time, which might otherwise affect the computations, will thus be made apparent."

It would seem that an arbitrary distinction between homogeneous and heterogeneous sludges as to which method of analysis should be used has been made here. This becomes clear when we apply the logarithmic analysis for heterogeneous sludges to a homogeneous sludge such as the Filter-Cel test illustrated in Figures 1 and 2. By means of Figure 2 it was demonstrated that a value of m resulted when log V was plotted against log Θ. Equation 5, utilizing the same method of plotting, indicates that the slope of the line in Figure 2 is also equal to $(1 + t)/(2 + t)$, as well as $1/(m + 1)$, or 0.591. Solving this for t, we find $t = 0.445$. Therefore, no actual difference exists between the concept of scouring effect and the older assumption that rate of flow is a power function of the volume of filtrate, in so far as the method of analysis is concerned. Baker found no assignable exponent of V able to reduce the curvature of Figure 1. Considerable doubt therefore arises as to whether the logarithmic analysis is a true measure of scouring effect, even should the effect exist. In this respect Underwood (*29*) has indicated that the concept of scouring effect possesses a doubtful theoretical basis, and shows how a value of t other than zero may arise merely through neglect of cloth resistance. A further illustration of the ambiguity surrounding the treatment to be used is seen in the illustrative example of Badger and McCabe (*4b*). They utilize the logarithmic analysis for heterogeneous sludges in the treatment of a series of tests upon a sludge of unstated composition. It may be easily verified that the data thus employed comprise the filtration tests of Almy and Lewis (*2*) upon chromium hydroxide, which, being a homogeneous sludge, should have been analyzed by means of a plot of V^2 *vs.* Θ.

SPERRY'S THEORIES AND EQUATIONS

Opposed to the Lewis equations are the treatments of Sperry (*22, 23, 26*), Alliott (*1*), Hinchley, Ure, and Clarke (*15, 16*), van Gilse, van Ginneken, and Waterman (*10*), Underwood (*27–29*), and others. These workers agree in the belief that filter-base resistance must be an integral part of the filtration equation. While the Lewis treatment recognizes the existence of press and filter-base resistance, its effect per se is not included in the integrated equations, although the method by which it might be treated has been indicated by the addition of a term to one of the simpler differential expressions. For this reason the Lewis equation has been criticized by a number of workers. If, however, such fault does exist, it is not due directly to neglect of cloth resistance. In this respect the Lewis equation is easily misinterpreted. In order to avoid what has always been regarded as a complicated phenomenon, the Lewis equation seeks to dismiss the effect of cloth resistance by the ingenious plan of defining the pressure, P, to which $dV/d\Theta$ through the cake is proportional, as the pressure drop through the cake alone. Thus Weber and Hershey were careful to distinguish P from the total measured pressure drop, P_t. Although it is impossible to measure P, the main criticism that may be made of this procedure is that P is apparently thought to remain fairly constant in the subsequent treatment. Weber and Hershey state that "although $P_t - P$ (pressure drop through the filter base) is not a constant at the beginning of the filtration, it seems probable that by the time the total pressure (P_t) has been adjusted to a constant value, changes in the pressure due to press resistance will have become negligible, and that for most of the run a constant total pressure will indicate a constant value of P."



Courtesy of D. R. Sperry & Co.

FILTER PRESSES USED IN MANUFACTURE OF MALT SIRUP

This picture of the filtration process does not appear quite correct, however, in the light of the following reasoning. At the instant filtration begins, it seems reasonable to believe that the entire pressure drop, P_t, must be absorbed by the filter base and press leads, and hence P must be zero. Thereafter throughout the filtration the ratio $P/(P_t - P)$ is identical with the ratio of cake resistance to press and filter-base resistance. If press and filter-base resistance remain reasonably constant, it is evident that the ratio of cake resistance to (press plus filter-base resistance), and hence the ratio $P/(P_t - P)$ must continuously increase, so that P approaches P_t as a limit when filter-base resistance becomes negligible compared to that of the cake.

It would appear from this that, instead of being a constant, P is a variable, which might be expressed as a function of V, so that when $V = 0$, $P = 0$. Although this would increase still more the complexity of the integration, it seems probable that the intention to circumvent the difficulty of treating filter-base resistance directly could then be successfully attained.

Other workers have chosen to use the entire and easily measured constant-pressure drop through both the cake and the supporting cloth in their equations, and hence have included the resistance of the filter base. By this means Underwood was able to show that an equation of the form:

$$r = r'(1 + \beta P)$$

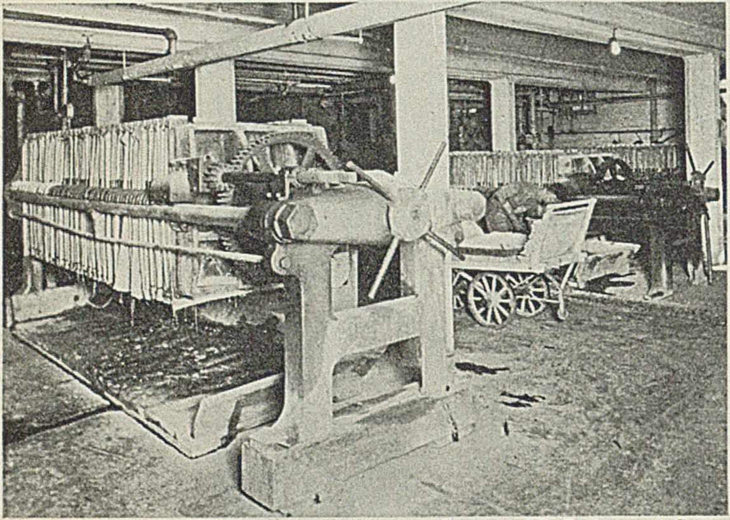
described approximately the variation in resistance for the chromium hydroxide sludge of Almy and Lewis. More recently van Gilse, van Ginneken, and Waterman (*12, 13*) have indicated that the same expression describes the variation in filtration resistances of various types of charcoal suspensions. It cannot be said, however, that any notable success has been attained by the use of such equations. The latter workers, whose papers form the latest contribution to the subject, after successfully treating filtrations performed in a small suction filter, were forced to conclude, when they turned to tests in a press of the plate and frame type, that their previous equations successfully accounting for cloth resistance no longer held.

Underwood (*27*) had indicated possible reasons for this failure of equations as early as 1926. His conclusions, based on exhaustive analysis of the available data, were as follows:

> (1) The "rational" filtration formula as proposed by Sperry, and modified by Alliott, and by Hinchley, Ure, and Clarke, assumes that the rate of flow is proportional to the first power of the pressure through both the filter cake and the filter cloth.
>
> (2) The data yield satisfactory agreement with these formulas in cases where the resistance of the filter base is negligible compared with that of the filter cake.

> (3) Where these conditions are not fulfilled, there is a lack of agreement which can be explained by the assumption that the flow through the filter cloth is not proportional to the first power of the pressure but to some other power.

He showed that an experimental basis for this assumption existed in the results secured by Hinchley, Ure, and Clarke when pure water was run through clean filter cloths, monel metal filter cloths, and filter cloths covered with thin layers of precipitate. In a more recent paper (*29*) he reviewed the results of a number of workers which appear to support this belief.



Courtesy of D. R. Sperry & Co.

Filter Presses Used in Manufacture of Zeolites

Hinchley, Ure, and Clarke had observed that, when pure water was passed through a metal filter cloth, the rate of flow varied as the square root of the pressure. On the other hand, the rate of flow through a clean cotton filter cloth was found to be more nearly proportional to the square of the pressure. Through thin layers of cake, P was found to increase much more rapidly than the rate of flow (proportionately to $\sqrt{P}$). However, as the layers became thicker, the increase in P became less and approached a linear proportionality. Hatschek (*14*) had observed a similar phenomenon in which the rate of flow through a clean filter cloth varied almost linearly with the pressure until an inflection point was reached. Here the rate of flow suddenly but momentarily increased, and thereafter increased less rapidly than the first power of the pressure. As thin layers of precipitate were added to the cloth, the point of inflection rapidly moved beyond the experimental range of pressure.

The early work of King (*18*), using columns of packed wire gauze, sands of various sizes, and prepared sections of sandstone, indicated that rate of flow increased more rapidly than the first power of the pressure.

It is only in comparatively few cases that an adherence to Poiseuille's law has been reported. Bigelow (*7*) has shown that the first-power proportionality between P and rate of flow holds for parchment and collodion membranes. Both Bigelow and Brunhes (*9*) have shown that it holds for porous earthenware, and Schaum (*21*) for a porous plate made from kieselguhr containing a siliceous binder.

Sperry (*25*) was able to show that the rate of flow of pure water through a half-inch (1.3-cm.) cake of kieselguhr in a filter press was exactly proportional to the first power of P, provided that it had been previously subjected to high pressure and was submitted to decreasing values of pressure during the test.

Although the evidence at first sight appears to be contradictory, reasonable explanations for the different types of flow can be deduced. Both Underwood (*29*) and Pickard (*20*) have indicated that the proportionality of flow approaching the square root of P may be due to turbulent flow through the pores of a screen; the proportionality to the square of pressure exhibited by cotton cloth may be due to the mechanical stretching which would tend to open its pores as increasing pressure causes it to bulge in the spots unsupported by drainage numbers.

Underwood has developed equations to cover the three general cases wherein rate of flow in the early stages may be proportional to $\sqrt{P}$, P, or P^2. In applying these equations to data in the literature, he concluded that the rate of flow through the cloth and initial layers of cake in the work of Hinchley, Ure, and Clarke upon calcium carbonate and magnesium carbonate had varied as the square of the pressure. A similar analysis of the work of Almy and Lewis led, on the other hand, to the conclusion that flow through a filter cloth covered with a thin layer of chromium hydroxide was proportional to the square root of the pressure.

While an intelligent criticism of Underwood's conclusions cannot be made at this time, it may be pointed out that the experiments of King (*18*), of Waterman and Dauvillier (*33*), and more recently of van Gilse, van Ginneken, and Waterman (*11*) show that, when pure water is run through a septum at constant pressures, the time required for a given quantity to pass through continues to increase indefinitely. Such experiments indicate that it is the resistance to flow of water which varies. It is evident that had this phenomenon been present in the work of Hatschek, or that of Hinchley, Ure, and Clarke, its effect would not have been detected in their method of experimentation, and might account for some of the results obtained.

Concept of Specific Resistance

In so far as can be ascertained, the question has never been raised as to whether existing filtration equations rest upon a valid basis. It would seem, in view of the rather universal failure of equations to describe the entire filtration cycle, that this possibility should not be overlooked. In the opinion of the writers it is possible to show that one of the most important assumptions upon which the derivations of general filtration equations have been based in the past possesses no theoretical, and at best only an insecure experimental basis. Reference is made to the concept of specific resistance and the mechanism of the filtration process as at present postulated by this concept. In order to make clear the reasons which appear to invalidate this concept, it will be necessary to review the assumptions upon which the derivations of filtration equations are commonly based.

It has been well agreed that the differential rate of filtrate flow at any time during the filtration process is directly proportional to the pressure producing it, and inversely proportional to the resistance encountered. Written as:

$$\frac{dV}{d\Theta} = \frac{P}{R}$$

this is a simplified form of Poiseuille's law. In actual practice this equation is of little value because it is difficult to measure the rapidly changing rates of flow during a filtration. It is the integrated form which is useful as a law of filtration.

If we confine ourselves to the consideration of rigid, noncompressible granular particles, it is evident that the resistance to flow offered by a layer of solids of unit thickness should be doubled for a layer of twice that thickness, provided the relative arrangement of particles is the same in both layers, and the resistance of the supporting septum is negligible. In a filtration the solids coming in contact with the filtering medium are uniformly distributed in the prefilt, so that, when the cake is noncompressible, a constant proportionality exists between the amount of filtrate expelled from the cake and the volume or weight of solids added to it. It thus becomes possible to express the variable resistance, R, in terms of filtrate volume. In the Lewis equation, for example, R is given as:

$$R = \frac{r''vP^s}{A^{2+\iota}} \int \left(\frac{dV}{d\Theta}\right)^{\iota} dV \qquad (6)$$

for the general case. For the noncompressible homogeneous material we are considering, this would simplify to:

$$R = \frac{r''vV}{A^2} \qquad (7)$$

It is now possible to substitute this into the simple Poiseuille expression and perform an integration, yielding:

$$V^2 = \frac{2A^2P\Theta}{r''v} \qquad (8)$$

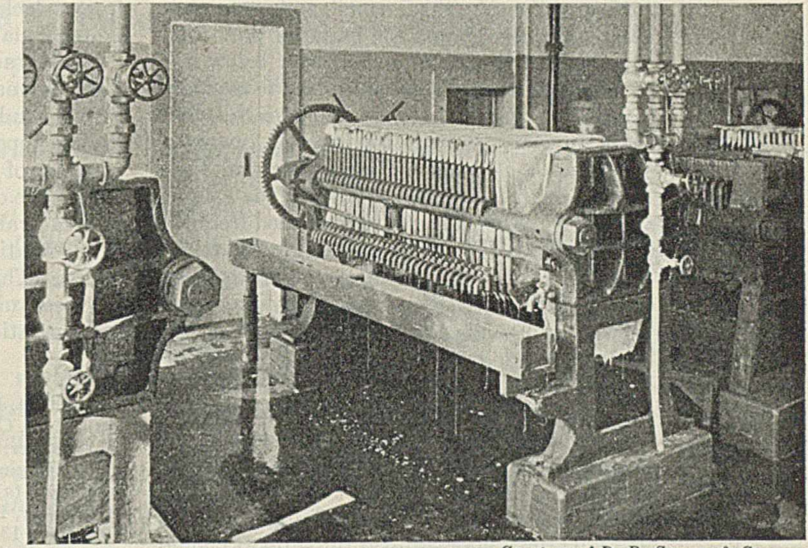
The form of equation which results in the Lewis treatment by integration of the more general expression has been shown in Equation 4.

Equation 8 predicts from purely theoretical considerations that the integrated form of the filtration equation for noncompressible solids is a parabola. Aside from the neglect of cloth resistance, the correctness of the fundamental assumptions upon which it is derived cannot be questioned. However, the existence of materials which evidence completely noncompressible behavior during the filtration process has never been demonstrated, and neither has perfect agreement between the equation and experimental data.

The question arises as to whether extending the concept of specific resistance from the ideal noncompressible to the highly or even slightly compressible materials of actual experience, is a justifiable procedure.

Lewis and his co-workers have not attempted to picture the mechanism of the filtration process by means of which they arrive at Equation 6. Underwood and also van Gilse, van Ginneken, and Waterman (*10*) have done so, however, for similar treatments. According to Underwood (*30*): "For compressible inelastic sludges, the resistance at any point in the cake will be the resistance corresponding to the highest pressure which at any time has been applied at that point. For filtration at constant pressure this maximum pressure will be the pressure of filtration, since every layer of cake is subjected to this pressure at the moment it is deposited. The resistance will therefore be constant throughout the cake, and will be equal to rP^s." Van Gilse, van Ginneken, and Waterman (*10*), as well as Pickard, have expressed similar views. It might be well to restate these as follows: As the suspended solids arrive at the filtering surface or deposition zone of a filter cake, they are impressed upon it with the entire force of the total pressure drop. Consequently they immediately contribute an additional resistance to filtrate flow equal to the value assigned to them by the concept of specific resistance, while the resistance of the cake previously deposited is supposed to remain unchanged.

It is hard to reconcile this picture of the filtration process with the appearance of a filter cake formed from a highly compressible material such as ferric hydroxide. As is well known, the cake formed by such materials is hard and relatively dry at the surface adjoining the filter cloth. At a distance of several millimeters from the cloth it becomes much softer and rapidly degenerates into a soupy mass which exhibits but little more consistency than the original prefilt. An analysis of the moisture content of the various layers bears out this observation; ferric hydroxide, for example, varies from 97 to 98 per cent moisture at the deposition zone, to 85 per cent in the layer adjoining the cloth. Now the decrease in moisture content throughout a filter cake may be considered as proportional to the decrease in the volume of the voids, or channels for filtrate flow. According to Poiseuille's law, the resistance to flow through a collection of capillary tubes should vary inversely as the fourth power of the radius, provided the number of tubes remains constant. A logical basis is therefore provided for believing that a large part of the resistance of such a cake is located in the layer adjoining the cloth, and very little or none in the freshly deposited layers.



Courtesy of D. R. Sperry & Co.

FILTER PRESSES USED IN MANUFACTURE OF COMPRESSED YEAST

Although the case of ferric hydroxide is extreme, a more or less unequal distribution of resistance must exist in a similar manner in every filter cake which is composed of a material to any extent compressible. This is borne out by the variation in moisture content, both throughout the cake and in cakes filtered at different pressures. In fact, it can be shown that the variation in moisture content of filter cakes formed at different pressures is proportional to the degree of compressibility, and constitutes a good qualitative means of predicting whether a material is compressible or noncompressible in its behavior. It is therefore clear that, if the variation of moisture content throughout a filter cake is to be accepted as evidence of a large change in the resistivity per unit amount of solids, we must conclude that the mechanism of cake formation as previously described cannot be true. It would appear that a considerable portion of the increase in resistance per unit volume of filtrate arises, not from the addition of new solids to the surface of the cake, but from a contraction in the pore volume of the solids already deposited. Since the amount of this contraction will be proportional to the deforming stress or pressure exerted at any particular point in the cake, the question arises as to how the deforming stress varies throughout the cake.

It would seem that the filtration pressure itself can have no effect upon the shape of individual particles, although this is contrary to the opinion implied by some workers. This is easily visualized by imagining the effect of an increasing hydrostatic pressure upon a freely suspended sponge. It is only when this pressure becomes unbalanced that deformation of the sponge can take place. In the filtration process an unbalanced pressure results from the movement of liquid relative to the suspended solids, and this occurs only when the latter are suddenly arrested in their free motion with the liquid by impinging upon the filter medium.

The magnitude of this unbalanced pressure is equal to the kinetic energy lost by a column of water of equal area, when the column is deflected from its course by the arrested particle. At the surface of the cake this is small, and serves only to hold the particle in place against the material previously deposited. In the layers of particles immediately below it, a greater amount of kinetic energy is given up by the capillary streams, since flow must become faster in order for the same quantity of liquid to pass through the smaller openings. Thus each particle is acted upon by an unbalanced force equal to the cumulative thrust of all particles in the column above it, and opposed by an equal force transmitted from the supporting septum upwards through the column of particles below it. If the particles are deformable, they tend to fill up the voids. This in turn requires adjacent capillary streams of liquid to travel with still higher velocity. It is apparent therefore that the magnitude of this viscous drag rapidly increases in the layers near the cloth. If we try to picture the deforming stress or pressure in terms of cake thickness, we obtain a curve which begins with almost zero pressure at the deposition zone, increases but slightly as the center region of the cake is approached, and then may start to increase with exponential rapidity through the layer adjoining the cloth until it reaches the full filtration pressure at the support behind the cloth.

Only one citation can be found in the literature which adequately describes the pressure relations as postulated above. This is due to Bloomfield (*8*) who states:

> The total thrust (or the "pressure") transmitted from the fluid prefilt to the solid support behind the filtering medium is communicated in two distinct ways: (*a*) through the skeleton of solid particles forming the cake, and (*b*) through the fluid in the interstices. It is fairly obvious that the hydrostatic pressure of the fluid must diminish progressively as it passes through the cake, from the total pressure P to zero at the back of the filtering medium. It does not appear to be so clearly recognized that the thrust transmitted by the solid skeleton must be complementary to this, varying from zero at the surface of the cake, to P at the back of the filtering medium.

It should be fairly clear from the above considerations that the distribution of resistance from deposition zone to cloth surface in a filter cake is a far more complex matter than has previously been supposed. When we recall that Hatschek, Munning (*19*), Hinchley, Ure, and Clarke, and others have observed that, when pure water is passed through a filter cake, the resistance varies with the pressure, the rate of flow, the total volume of liquid passing through, and the time during which it is subjected to pressure, the problem of expressing R in terms of V from theoretical considerations alone appears too complex to admit of solution.

The position in which we are placed becomes quite clear. For rigid noncompressible solids it is possible to derive an equation by integration of the Poiseuillian differential expression which is quite valid. For compressible materials, however, we are unable to write R in terms of the variables affecting it. It is therefore impossible to integrate the equation upon a valid theoretical basis, and we are unable to predict with assurance what the exact nature of the relation between V and Θ should be.

Experimentally it is found that the data for all types of materials exhibit a similar behavior in the latter stages of a filtration. Moreover, the relation between V and Θ is undoubtedly parabolic, and hence resembles to some extent the equation for ideal noncompressible solids. Nevertheless, the complete identification of the integrated equations with experimental data has never been proved. It must therefore be admitted, in view of the objections which can be raised, that the application of theoretical equations to actual filtration processes rests upon a doubtful theoretical basis. In this event it becomes possible that the disagreement between experimental data and equations may arise, not from a failure to establish uniform filtering conditions in the early stages of a test, nor from the failure to obey Poiseuille's law, but simply from a lack of knowledge as to the exact form of the integrated equations which govern the process.

The attack upon the problem should therefore be most logically made from an experimental angle, by means of a careful study of the individual behavior of various materials in the hope that type equations may be found which are capable of accurately describing the entire process. A knowledge of the exact nature of such equations should prove of great value, since from their differential form the nature of the relation between R and P, V and $dV/d\Theta$ might be deduced. This knowledge in turn might shed much light upon the mechanisms of the phenomena occurring in this important unit operation of chemical engineering.

LITERATURE CITED

(1) Alliott, E. A., *J. Soc. Chem. Ind.*, 39, 261T (1920).
(2) Almy, C., and Lewis, W. K., J. IND. ENG. CHEM., 4, 528 (1912).
(3) Badger, W. L., and McCabe, W. L., "Elements of Chemical Engineering," McGraw-Hill, 1931.
(4) *Ibid.*, (*a*), p. 457; (*b*), pp. 460-4.
(5) Baker, F. P., J. IND. ENG. CHEM., 13, 610 (1921).
(6) *Ibid.*, 13, 1163 (1921).
(7) Bigelow, S. L., *J. Am. Chem. Soc.*, 29, 1675 (1907).
(8) Bloomfield, A. L., *Trans. Inst. Chem. Engrs.* (London), 3, 38 (1925).
(9) Brunhes, J., Thèses de la faculté des sciences de Toulouse, Douladouré-Privat, Toulouse, 1881.
(10) Gilse, J. P. M. van, Ginneken, P. J. H. van, and Waterman, H. I., *J. Soc. Chem. Ind.*, 49, 444T (1930).
(11) *Ibid.*, 49, 483T (1930).
(12) *Ibid.*, 50, 41T (1931).
(13) *Ibid.*, 50, 95T (1931).
(14) Hatschek, E., *J. Soc. Chem. Ind.*, 27, 538 (1908).
(15) Hinchley, J. W., Ure, S. G. M., and Clarke, B. W., *Ibid.*, 45, 1T (1926).
(16) Hinchley, J. W., Ure, S. G. M., and Clarke, B. W., *Trans. Inst. Chem. Engrs.* (London), 3, 24 (1925).
(17) Jewett, E. E., and Montonna, R. E., *Chem. & Met. Eng.*, 34, 86 (1927).
(18) King, U. S. Geol. Survey, *19th Ann. Report*, II, 59 (1897-8).
(19) Munning, Master's Thesis, Mass. Inst. Tech., 1921.
(20) Pickard, J. A., *Ind. Chemist*, 4, 186 (1928).
(21) Schaum, *Kolloid-Z.*, 34, 1 (1924).
(22) Sperry, D. R., *Chem. & Met. Eng.*, 15, 198 (1916).
(23) Sperry, D. R., *Ibid.*, 17, 161 (1917).
(24) Sperry, D. R., J. IND. ENG. CHEM., 13, 1163 (1921).
(25) Sperry, D. R., *Ibid.*, 18, 276 (1926).
(26) Sperry, D. R., *Ibid.*, 20, 892 (1928).
(27) Underwood, A. J. V., *Trans. Inst. Chem. Eng.* (London), 4, 19 (1926).
(28) Underwood, A. J. V., *J. Soc. Chem. Ind.*, 47, 325T (1928).
(29) Underwood, A. J. V., *Proc. World Eng. Congr. Tokyo, 1929*, 31, 245 (1931).
(30) Underwood, A. J. V., *Ibid.*, p. 258.
(31) Walker, W. H., Lewis, W. K., and McAdams, W. H., "Principles of Chemical Engineering," McGraw-Hill, 1923 and 1927.
(32) *Ibid.*, p. 371.
(33) Waterman, H. I., and Dauvillier, A., *Rec. trav. chim.*, 45, 628 (1926).
(34) Waterman, H. I., and Gilse, J. P. M. van, *Ibid.*, 43, 757 (1924).
(35) Weber, H. C., and Hershey, R. L., IND. ENG. CHEM., 18, 341 (1926).

RECEIVED July 25, 1932. This paper is abstracted from part of a thesis submitted by B. F. Ruth in December, 1931, to the faculty of the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of doctor of philosophy.

Effect of Accelerators and Antioxidants on Electrical Characteristics and Water Absorption of Vulcanized Rubber Insulation

J. H. Ingmanson, C. W. Scharf, and R. L. Taylor, Bell Telephone Laboratories, New York, N. Y.

Typical 30 per cent vulcanized-rubber insulating compounds have been prepared in which were incorporated separately ten well-known accelerators and twelve commercial antioxidants. The moisture absorption, specific resistivity, specific a. c. conductance, dielectric constant, and power factor for each have been determined both in the dry condition and after immersion in distilled water at 70° C. for 5 days.

The data obtained indicate that the choice of accelerator or antioxidant among those tested is not critical as regards moisture absorption, but may be somewhat critical as regards electrical characteristics imparted to a high-grade soft rubber insulation. The variations in moisture-absorbing characteristics of the compounds, which are attributed to the particular accelerator or antioxidant used, are not satisfactory criteria for judging degree of electrical stability. It is shown that power factor increases with time of cure in compounds containing thiurams as accelerators and 1.35 per cent of sulfur.

Of the accelerators tested, highest resistivity values have been obtained on compounds accelerated with thiurams. The variations in the electrical characteristics of the compounds containing antioxidants cannot be attributed directly to differences in chemical structure of the antioxidants.

THE major improvements effected in manufactured rubber articles during recent years can be largely attributed to the introduction of accelerators and antioxidants into rubber compounds. Despite the well-known advantages resulting from the use of these materials in rubber used for various commercial purposes, the introduction of organic accelerators and antioxidants into insulating stocks is only now becoming general.

The hesitancy of the wire trade to accept these materials has been partly due to the fact that technical societies' specifications prohibited their use. Another important reason is undoubtedly the fact that information has not been available regarding the electrical characteristics imparted by these materials to insulation stocks under the varied conditions of required service.

The work herein reported, which is a continuation of studies carried on in this laboratory some years ago under the direction of A. R. Kemp, was undertaken for the purpose of determining the effect that various representative commercial accelerators and antioxidants have upon the electrical characteristics of a typical rubber-insulating compound.

SURVEY OF PREVIOUS WORK

In 1925 Curtis and McPherson (*2*) showed that increased resistivity, lowered power factor, and lowered specific inductive capacity could be obtained in the case of pure gum stocks by vulcanizing with a combination of tetramethylthiuram disulfide and sulfur rather than sulfur alone. In a later paper the same authors with Scott (*3*) showed that dielectric constant and power factor vary over a wide range, depending on percentage of combined sulfur. Kemp (*5*) has shown that the most desirable electrical characteristics are obtained with low sulfur ratios in the case of soft rubbers, and with very high sulfur ratios for hard rubber. Aizawa and Tacheuchi (*1*) have shown that the maxima of these characteristics are shifted with increasing temperatures in the direction of greater combined sulfur ratios.

Since the use of accelerators in soft rubber compositions makes it possible to obtain maximum physical properties with lower sulfur ratios, it follows that improved electrical characteristics may be expected to result from their use.

Kemp (*4*) showed that the physical properties and useful life of rubber-insulated wire used by the telephone industry have been greatly extended, largely as a result of the use of accelerators and antioxidants in the rubber. This was the first work reported involving an evaluation of the electrical characteristics of antioxidants.

CHOICE AND PREPARATION OF MATERIALS FOR TEST

There are available commercially today over fifty organic accelerators and at least a score of antioxidants for use in rubber. It has been necessary to limit the number of materials investigated at this time. Accordingly, ten well-known accelerators and twelve antioxidants have been selected as representing several types of these materials. The electrical characteristics of a 30 per cent rubber-insulating compound in which each antioxidant and accelerator was incorporated separately have been determined in a dry and wet condition. The base compounds given in Table I are modeled after A. S. T. M. and A. R. A. 30 per cent compound requirements.

TABLE I. BASE COMPOUNDS

COMPOUND FOR ACCELERATOR TESTS		COMPOUND FOR ANTIOXIDANT TESTS	
Smoked sheets	31.00	Smoked sheets	31.00
Whiting	32.35	Whiting	32.35
Zinc oxide	32.00	Zinc oxide	32.00
Paraffin	2.00	Paraffin	2.00
Sulfur	1.35	Sulfur	1.35
Accelerator	0.30	Tetramethylthiuram monosulfide	0.30
		Antioxidant	1.00

For testing the accelerators, ten compounds were prepared, each containing 0.3 part of an accelerator. Similarly, twelve other compounds were prepared for testing the antioxidants, each compound containing 1.0 part of an antioxidant. The base compound containing the antioxidants was the same as was used for the accelerators, except that 0.3 part of tetramethylthiuram monosulfide was added in all cases to give shorter curing time.

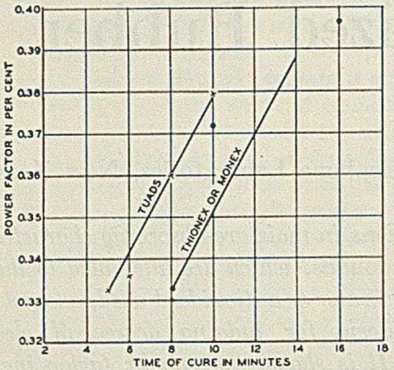


FIGURE 1. CHANGE IN POWER FACTOR WITH TIME OF CURE IN VULCANIZED RUBBER ACCELERATED WITH THIURAM SULFIDES

Electrical test sheets, 15 cm. square and 0.128 cm. thick, were vulcanized in a mold at 135° C. Duplicate sheets were prepared at the optimum cure as determined by tensile.

The weighing of the ingredients, milling, and the preparation of the molded sheets were carried out with painstaking care and minute attention to details to insure uniformity in the test sheets.

TESTING PROCEDURE AND METHOD OF ELECTRICAL MEASUREMENT

The electrical test sheets were dried over calcium chloride several days after being vulcanized. They were then cleaned by wiping the surface with petrolic ether. After the cleaning operation, measurements were carried out in the following order: thickness, area, capacitance and conductance, insulation resistance, and original weight of sheets; and weight, capacitance and conductance, and insulation resistance after immersion in distilled water for 5 days at 70° C.

The temperature ranged from 23° to 25° C. and the relative humidity from 40 to 60 per cent during the tests.

MEASUREMENT OF AREA AND THICKNESS. The same electrodes were used for each sheet tested. The area of the guarded electrode was 98.4 sq. cm.

The thickness of the specimens was measured with a Schopper micrometer which could be read to ±0.0002 inch (0.0005 cm.). Ten measurements were made on a systematic pattern over the sheet within the space covered by the upper electrode. The average thickness of the 48 sheets was 0.128 cm., and the percentage deviation of the mean, 0.6. The percentage deviations of the mean of the ten thickness measurements made on the single sheets averaged about 0.9 per cent.

DIELECTRIC CONSTANT, A. C. CONDUCTANCE AND POWER FACTOR. Measurements of dielectric constant and conductance were made on a shielded capacitance bridge described by Shackelton and Ferguson (*6*). This bridge equipment consists of a bridge balance unit and a capacitance-resistance standard, together with an oscillator and a detector. The balance unit consists of shielded input and output transformers, two equal shielded resistance ratio arms, a variable input attenuator, two variable balancing air condensers, a conductance compensator, and ratio-arm and impedance-arm reversing switches. The resistance-capacitance standard consists of an *AD* resistance of five ten-step decades, an adjustable *CD* resistance, a mica decade box of two nine-step decades, two ten-step air decade condensers, one continuously variable air condenser, a direct capacitance switch, and a switch to ground either the *C* or *D* point of the bridge. The oscillator and detector were standard Western Electric equipment.

The capacitance was measured to 0.1 micromicrofarad and the conductance to 10^{-10} mhos. All measurements were made at a frequency of 2000 cycles per second.

A toolmaker's surface plate was used as the lower electrode. The upper electrode consisted of a $4^1/_2$-inch (11.4-cm.) brass ring, $^3/_{16}$ inch (0.48 cm.) high, filled with mercury surrounded by a mercury guard ring of the same height and of inside diameter $4^5/_8$ inches (11.75 cm.). The brass ring was beveled on the outside to a $^1/_{64}$-inch (0.04-cm.) edge to obtain better contact with the sheet. Care was taken to fill the ring to the same height with mercury for each measurement in order that the pressure should be the same on each sheet.

The dielectric constant was calculated using the equation:

$$K = \frac{C \times t}{0.0885A}$$

where C = capacitance, micromicrofarads
t = thickness of sheet, cm.
A = area of guarded electrode, sq. cm.

The specific conductance is given by the equation:

$$\text{sp. } G = \frac{Gt}{A}$$

where G = conductance, mhos

The power factor is given by the equation:

$$\text{P. F.} = \frac{G}{2\pi f C}$$

where C = capacitance, farads
f = frequency, cycles per second

The area is precise to 0.5 per cent; the individual thickness measurements, to 0.4 per cent; and the capacitance measurements, although individually precise to 0.02 per cent, may be considered reproducible within 0.1 per cent. The precision of the dielectric constant will then be about 0.7 per

TABLE II. ELECTRICAL CHARACTERISTICS OF VULCANIZED RUBBER COMPOSITIONS CONTAINING VARIOUS ANTIOXIDANTS

ANTIOXIDANT	MOISTURE ABSORPTION	SP. A. C. CONDUCTANCE Dry	SP. A. C. CONDUCTANCE Wet	DIELECTRIC CONSTANT Dry	DIELECTRIC CONSTANT Wet	SP. RESISTIVITY Dry	SP. RESISTIVITY Wet	POWER FACTOR (× 10²) Dry	POWER FACTOR (× 10²) Wet
	%	*Mhos/cm.³ × 10¹²*				*Ohms/cm.³ × 10⁻¹⁵*			
Neozone D or Age-Rite powder (phenyl-β-naphthylamine)	2.83	16.1	74.8	4.20	5.42	3.20	1.40	0.344	1.241
Age-Rite resin (aldol-α-naphthylamine)	3.03	16.6	83.3	4.26	5.49	3.85	1.15	0.350	1.365
Age-Rite white (*sym*-di-β-naphthyl-*p*-phenylenediamine)	2.98	14.7	61.8	4.15	5.26	5.70	1.77	0.318	1.055
Zalba (formula unknown)	2.09	19.6	89.6	4.30	5.72	1.90	0.69	0.409	1.410
Antox (butyraldehyde aniline derivative)	2.43	16.9	96.5	4.27	5.60	0.72	0.16	0.356	1.545
BLE (amine reaction product)	2.78	16.6	93.8	4.17	5.74	3.30	0.59	0.357	1.470
Neozone standard (phenyl-α-naphthylamine, *m*-toluenediamine, and stearic acid)	2.47	15.9	53.6	4.18	5.17	5.70	1.78	0.342	0.932
Oxynone (*Unsym*-diaminodiphenylamine)	2.37	17.6	52.7	4.15	5.04	4.75	1.36	0.380	0.940
Resistox (aldol aniline)	2.88	17.5	92.3	4.24	5.56	3.85	1.39	0.370	1.488
Stabilite (diphenylethylene diamine)	2.10	16.8	98.8	4.27	5.71	0.85	0.79	0.352	1.555
V. G. B. (acetaldehyde ethylene diamine)	2.91	18.9	92.3	4.22	5.50	5.00	1.58	0.404	1.507
Stabilite Alba (di-*o*-tolylethylene diamine)	2.26	16.1	102.3	4.31	5.68	1.85	0.82	0.335	1.619

TABLE III. ELECTRICAL CHARACTERISTICS OF VULCANIZED RUBBER COMPOSITIONS CONTAINING VARIOUS ACCELERATORS

ACCELERATOR	MOISTURE ABSORPTION	SP. A. C. CONDUCTANCE Dry	SP. A. C. CONDUCTANCE Wet	DIELECTRIC CONSTANT Dry	DIELECTRIC CONSTANT Wet	SP. RESISTIVITY Dry	SP. RESISTIVITY Wet	POWER FACTOR ($\times 10^2$) Dry	POWER FACTOR ($\times 10^2$) Wet
	%	*Mhos/cm.*$^3 \times 10^{12}$				*Ohms/cm.*$^3 \times 10^{-15}$			
808 (aldehyde amine)	2.47	15.1	77.6	3.93	4.90	1.20	0.38	0.345	1.424
A-19 (condensation product of CHOH and Schiff base)	2.87	16.4	54.6	3.88	4.78	3.55	1.17	0.380	1.026
Vulcanol (thioketophenyldipropylpropylidine thiazine)	2.47	16.7	69.7	3.99	4.85	0.31	0.30	0.377	1.293
Trimene base (triethyltrimethyltetramine)	3.00	14.6	61.8	4.01	4.88	5.60	2.12	0.326	1.134
Monex or Thionex (tetramethylthiuram monosulfide)	2.31	17.4	77.9	4.20	5.44	4.70	1.83	0.372	1.289
Tuads (tetramethylthiuram disulfide)	2.32	16.9	90.3	4.22	5.61	5.75	1.55	0.360	1.444
Captax (mercaptobenzothiazole)	1.78	18.4	42.7	4.10	4.78	3.85	2.24	0.403	0.804
Altax (benzothiazildisulfide)	1.71	18.4	54.3	4.04	4.67	3.45	1.26	0.411	1.042
D. P. G. (diphenylguanidine)	3.02	15.0	65.7	3.90	4.96	0.49	0.29	0.347	1.190
Z-88 (formula unknown)	2.74	17.6	69.9	3.94	4.78	6.70	1.38	0.401	1.317

cent or approximately ±0.04 unit. Similarly, the percentage precision of the specific a.c. conductance will be in the order of 1.0 per cent and the power factor, 0.4 per cent. This gives the precision with which one sheet may be compared with another, but not absolute capacitance and conductance values, since not all stray currents and capacitances are accounted for with the electrodes used.

The variation between duplicate sheets of the same compound was less before immersion than after soaking for 5 days in water at 70° C. The average percentage deviation of the mean of the various electrical measurements before and after immersion is as follows:

	INSULATION RESISTANCE	DIELECTRIC CONSTANT	SP. A. C. CONDUCTANCE	POWER FACTOR
Dry	4.9	0.29	0.68	0.62
Wet	2.9	0.33	2.46	2.28

Because of the variation in physical characteristics which duplicate batches of vulcanized rubber of identical composition sometimes show, the compound containing tetramethylthiuram disulfide as an accelerator was prepared six times, duplicate sheets for electrical test being prepared from each compound. Duplication of electrical values was excellent and well within the limits of precision expressed above. It is believed that deviations of approximately the same order would result from similar tests on compounds containing the other accelerators and the antioxidants.

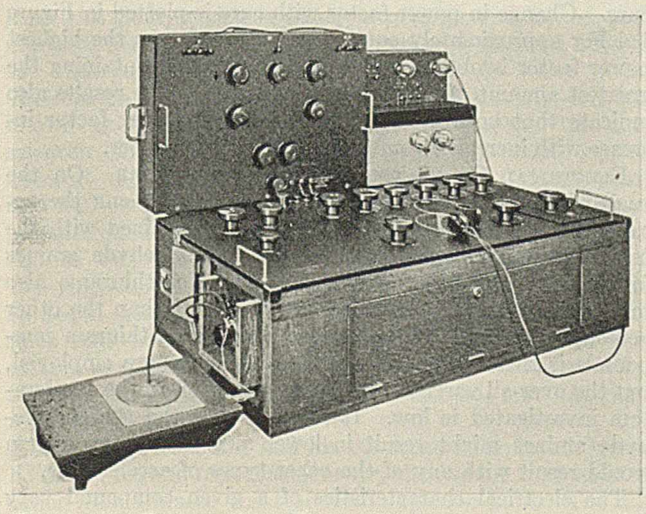


FIGURE 2. DOUBLE-UNIT CAPACITANCE AND CONDUCTANCE BRIDGE FOR MEASUREMENTS ON RUBBER SHEETS

INSULATION RESISTANCE. Insulation resistance measurements were made by the direct deflection method, using a 440-volt battery in series with the sample under test, a resistance of a megohm, and the galvanometer. The galvanometer was a Leeds & Northrup high-sensitivity galvanometer having a current sensitivity of 2×10^{-11} amperes per millimeter scale deflection; with a scale distance of one meter, resistances up to 2.2×10^{13} ohms could be measured. This apparatus is accurate within 5 per cent for normal deflections but the error may be greater than this when the deflections are small.

The same electrodes were used as in the case of the a. c. measurements.

The volume resistivity in ohms per centimeter cube is given by the formula:

$$\rho = \frac{RA}{l}$$

where R = resistance, ohms

DISCUSSION OF RESULTS

The test data obtained on sheets of the twelve compounds containing different antioxidants and on the ten containing different accelerators are listed in Tables II to V. Tables II and III give, respectively, the electrical test data on the antioxidant and accelerator series both before and after immersion in water at 70° C. for 5 days. Tables IV and V give the percentage change of the electrical characteristics resulting from the water exposure treatment.

TABLE IV. CHANGE IN ELECTRICAL CHARACTERISTICS OF VULCANIZED RUBBER CONTAINING VARIOUS ANTIOXIDANTS

(After immersion in water 5 days at 70° C.)

ANTIOXIDANT	MOISTURE ABSORPTION	A. C. CONDUCTANCE INCREASE	DIELECTRIC CONSTANT INCREASE	SP. RESISTIVITY DECREASE	POWER FACTOR INCREASE
	%	%	%	%	%
Neozone D or Age Rite powder	2.83	366	29	56	261
Age-Rite resin	3.03	402	29	70	290
Age-Rite white	2.98	320	27	69	231
Zalba	2.09	357	33	63	245
Antox	2.43	459	31	78	334
BLE	2.78	465	38	82	311
Neozone	2.47	239	24	69	172
Oxynone	2.37	200	21	71	147
Resistox	2.88	429	31	64	302
Stabilite	2.10	490	34	7	342
V. G. B.	2.91	388	30	68	273
Stabilite Alba	2.26	535	32	56	381

TABLE V. CHANGE IN ELECTRICAL CHARACTERISTICS OF VULCANIZED RUBBER CONTAINING VARIOUS ACCELERATORS

(After immersion in water 5 days at 70° C.)

ACCELERATOR	MOISTURE ABSORPTION	A. C. CONDUCTANCE INCREASE	DIELECTRIC CONSTANT INCREASE	SP. RESISTIVITY DECREASE	POWER FACTOR INCREASE
	%	%	%	%	%
808	2.47	414	25	69	312
A-19	2.87	233	23	67	170
Vulcanol	2.47	319	22	3	243
Trimene Base	3.00	324	22	62	247
Monex or Thionex	2.31	349	30	61	246
Tuads	2.32	434	33	73	301
Captax	1.78	132	17	42	99
Altax	1.71	195	16	64	154
D. P. G.	3.02	338	27	41	243
Z-88	2.74	298	21	79	228

MOISTURE ABSORPTION AND ELECTRICAL CHARACTERISTICS. The moisture absorption procedure involving immersion of specimens in distilled water maintained at 70° C. for 5 days is known to approximate the amount of moisture absorbed by soft vulcanized rubber over long periods of exposure to high humidity in severe use. Electrical characteristics of the specimens after having been subjected to the immersion test compare favorably with those which may be expected to obtain in insulations after similar severe usage.

The quantity of moisture absorbed is not a satisfactory criterion for judging electrical stability. High moisture absorption, however, should be cause for apprehension regarding ultimate electrical stability. The specimens containing Zalba, Stabilite Alba, and Stabilite absorbed the smallest quantities of water; yet their changes in electrical characteristics were of a comparatively high order for the most part. The specimens containing Age-Rite resin, Age-Rite white, V. G. B., and Resistox, on the other hand, absorbed larger quantities of moisture; yet their changes in electrical characteristics were no greater than in the case of the first three mentioned.

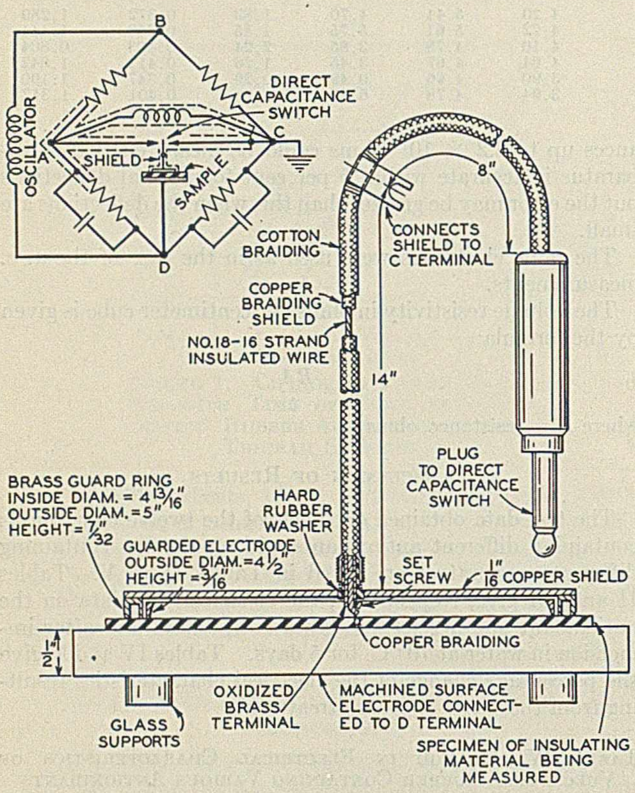


Figure 3. Shielded Electrode Arrangement for Measurements on Sheet Insulating Materials with Capacitance and Conductance Bridge

The bridge is connected as a "current bridge," the detector across the terminals *A* and *C*

On the other hand, in the case of accelerators the Altax and Captax specimens, which show the lowest moisture absorption, also show lowest increase in a. c. conductance, dielectric constant, and power factor, and a reasonably small decrease in specific resistivity. However, the D. P. G., Trimene Base, and A-19 specimens, which show the highest moisture absorption, show an increase in dielectric constant and power factor, and decrease in resistivity comparable with the specimens having the lowest moisture absorption.

Electrical Characteristics and Specifications. Insulation resistance requirements for A. S. T. M. 30 per cent rubber-insulated wires are based on a specific resistivity of 1.72×10^{15} ohm cm.^{3} for measurements made at 60° F. (15.6° C.). The specification designates coefficients to be used for reducing values obtained at temperatures other than 60° F. to an equivalent value at that temperature. Since measurements here were made at 23° to 25° C., a temperature coefficient of 1.40 to 1.50 should be applied. However, dividing the specific resistivity value of 1.72×10^{15} ohm cm.^{3}, which is used as a standard at 60° F., by an approximate temperature coefficient—namely, 1.45—a value of 1.19×10^{15} ohm cm.^{3} is obtained corresponding to test temperatures used in these experiments.

Among the materials tested, two accelerator and two antioxidant compounds fail to give an original resistivity of 1.2×10^{15} ohm cm.^{3}. After the immersion test, half of the antioxidant and five of the accelerator compounds failed to meet this value.

Failure to meet this value, however, does not mean that the insulation is not suitable for electrical use, since the specification requirements are many times higher than electrical considerations alone require.

The data indicate that the choice of accelerator and antioxidant from among those tested may be somewhat critical as regards meeting rigid specification requirements for insulation resistance.

Generally, it seems that more attention has been given to direct current than to alternating current methods for evaluating insulating materials. Alternating current measurements are reproducible and reliable and in a great many cases are to be recommended in preference to direct current; especially is this the case since, as the frequency is lowered, a. c. characteristics approach closely those of d. c. A classification or rating of the compounds on the basis of either a. c. or d. c. measurements would lead to approximately the same order of evaluation. This indicates that a. c. and d. c. measurements are comparable and that materials possessing superior a. c. characteristics are usually accompanied by a correspondingly high insulation resistance. It is believed that certain minor changes in the d. c. method might have improved the closeness of their correspondence, but in most cases it is believed that the a. c. conductance is the more reliable characterization of the materials than the d. c. resistivity.

Electrical Characteristics and State of Cure. Tests made on the compounds containing thiurams as accelerators showed that dielectric constant and a. c. conductance at a frequency of 2000 cycles per second increased with time of cure. Change in power factor with cure is plotted in Figure 1. For approximately equivalent states of cure the highest power factor is obtained with the accelerator containing the greatest amount of sulfur in the molecule. The results also indicate that both dielectric constant and power factor increase with increased combined sulfur in the rubber.

Electrical Characteristics and Structure. On the basis of the data recorded, it appears that, among the accelerators, the highest resistivity may be obtained with the use of thiurams, with the thiazoles and aldehyde amines following in the order named. The use of thiurams also results in slightly higher dielectric constants than the other accelerators tested. Power factor obtained on thiuram compounds is slightly lower than when thiazoles are employed, but the over-all variation in power factor for all the accelerators investigated is low. It appears that the use of aldehyde amines might result in lower a. c. conductance than would result with any of the other types of accelerators.

The electrical characteristics of a given compound vary with the amount of combined sulfur as shown in each of the curves in Figure 1. Accordingly, the order of evaluation of accelerators as given might be changed considerably by variations in degree of cure of the compounds.

Among the antioxidants tested, similar electrical characteristics were imparted to rubber compounds by such structurally different materials as acetaldehyde ethylene diamine, *sym*-di-β-naphthyl-*p*-phenylenediamine, and a mixture of phenyl-α-naphthylamine, *m*-tolylenediamine, and stearic acid.

Literature Cited

(1) Aizawa, S., Kimura, T., and Tacheuchi, T., *J. Inst. Elec. Eng.* (Japan), No. 485 (1928).
(2) Curtis, H. L., and McPherson, A. T., Bur. Standards, *Tech. Paper* 299 (1925).
(3) Curtis, H. L., McPherson, A. T., and Scott, A. H., Bur. Standards, *Sci. Paper* 560 (1927).
(4) Kemp, A. R., Paper presented before N. Y. Rubber Group of the American Chemical Society, May 20, 1931.
(5) Kemp, A. R., U. S. Patent 1,645,758 (1927).
(6) Shackelton, W. J., and Ferguson, J. G., *Bell System Tech. J.*, 7, 70 (1928).

Received August 10, 1931. Presented before the Division of Rubber Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931.

Production of Industrial Alcohol from Grain by Amylo Process

W. L. Owen, P. O. Box 1345, Baton Rouge, La.

The use of the amylo process for fermenting grain mashes undoubtedly owes its origin to the time-honored practice in the Orient of preparing alcoholic drinks by the use of mold fungi. In Japan, where the drink known as kojii is prepared from rice, or taka kojii where wheat bran is used, cultures of *Aspergillus oryzae* supply the diastase for the saccharification of the starch in the grain. In China, on the other hand, the predominating fungus in the mixture of microörganism used in preparing similar drinks is the *Amyloces Rouxii*, which belongs to the group of Mucors. In both cases the mold spores are developed on moist grain (either rice, wheat, or bran) and then transferred to the mash to be fermented. While *Aspergillus oryzae* has never been successfully used for the production of alcohol, owing perhaps to its faculty of producing a vigorous destruction of alcohol during the latter stage of fermentation, *Amyloces Rouxii* is capable of inducing a fairly efficient production of alcohol from sugar, and may be used both for the saccharification of starch and the fermentation of the sugar into alcohol. The Chinese, who employ this fungus in preparing their alcoholic drinks from starchy materials, start with a dough made from rice flour, which is made into cakes and mixed with aromatic herbs, and the whole covered with rice and allowed to undergo spontaneous fermentation. A white mold develops on the cakes; these are dried in the sun, and are known as Chinese yeast. Calmette (*5*) made the first scientific study of the microflora of this product, for, as a result of his extensive investigations of Chinese yeast in 1892, he found that a certain species of Mucor always predominated in this conglomeration of microörganisms, and to this species he gave the name *Amyloces Rouxii*. The Amylo process was developed by Calmette and Voidin at Seclin near Lille, and subsequently at Antwerp, and since that time this, or other similar processes, has been utilized in almost every country of the world where fermentations of amylaceous materials are carried out. At first *Amyloces Rouxii* was exclusively used in the process, but subsequently Calmette and his co-workers employed *Mucor B.*, *Mucor G.*, and *Rhizopus Delemar*, all of which were isolated either from Chinese yeast or from Japanese kojii. The advantages of these subsequently isolated cultures were their greater tolerance of alcohol and their lower production of acid.

Operation of Process

In the original process, the procedure in the fermentation of grain was carried out in the following stages: (1) conversion of the starch by heating under pressure; (2) saccharification of the starch by diastatic action of the mold; and (3) fermentation of the sugar by yeast.

The starch of the maize or other grain is gelatinized at 4 atmospheres pressure, and a small amount of sulfuric or hydrochloric acid is necessary in order to produce a thinner paste. It is important also that the gelatinized material be blown from the retorts at the end of the heating period at the maximum pressure in order to disrupt the grain effectively, so that the diastase can induce its efficient action upon the starch. It is often advisable to steep the grain in water prior to the cooking process, so that it can be given a preliminary softening prior to the action of the heat upon the starch. The coarsely crushed maize is usually agitated for one hour with 2 parts of water containing 0.6 to 0.8 part of concentrated hydrochloric acid to 100 parts of grain, which greatly accelerates the softening action.

From the converters the hot mash is blown through the discharge pipe into an intermediate vessel, and then to the fermenters. The purpose of the discharge into the intermediate vessel is to facilitate the complete disruption of the maize by the expansion of the cells under the sudden release of pressure. The mash is then boiled in the closed fermenters, and the escaping steam passed through the various connections for the purpose of sterilizing all of the avenues through which subsequent infection might be introduced. After the sterilization has been completed, the mash is cooled by running water over the outside of the fermenters, a positive pressure being maintained at all times to prevent the formation of a vacuum and the drawing of infection from the outside. To facilitate cooling of the mash, stirring devices are sometimes employed, and in lieu of these the mash is usually aërated vigorously during cooling to shorten the time required to bring the temperature where it can be seeded with the diastatic mold culture. When the mash has reached a temperature of 40° C., it is inoculated with a small quantity of the culture, usually about one gram of the spores. For the cultivation of the mold in the laboratory, a medium is used containing 16 to 17 per cent of starch which is introduced into culture tubes to a depth of 5 cm., or 250 cc. are introduced into liter flasks. These are sterilized at 30 pounds per square inch (2.1 kg. per sq. cm.) pressure for 20 minutes on two successive days. Another medium, consisting of rice grains moistened with water in the proportion of 1 cc. of water to 20 grams of rice, is prepared and sterilized as the liquid medium in flat layers in large flasks, using just sufficient rice grains to cover the bottom of the flasks. When starting large-scale operations, the tubes containing liquid mash are inoculated with the spores of the fungus and incubated at 38° C. for 4 or 5 days. At the end of this time the surface of the tubes is usually covered with the sporangia. The tubes are then thoroughly shaken to distribute the spores throughout the liquid. The contents of the tubes are then sprinkled over the sterile rice grains and the latter incubated for 8 days at 38° C. If, upon microscopical examination, this material is found to be free from bacteria, the inoculated seed are used to start a seed tub, containing one-tenth of the volume of mash to be fermented in the main fermenting tubs. The mash in the seed tub is sterilized by live steam for one hour at 110° C. and cooled to 39° C. before seeding.

After the inoculation of the mash with the mold, a current of air is maintained on the tub for 24 hours while the mold is developing; at the end of this time the entire mash is usually permeated with the mold. During the entire developing period the mash must be vigorously agitated either by air currents or mechanical stirring in order to prevent the formation of a film of spores on the surface. The surface growth is relatively weak in saccharifying power; the submerged cells are rich in the diastatic enzyme.

In carrying out the fermentation by the Amylo process, it is important that the temperature and the acidity be maintained at the optimum for this species. The acidity of the mash should not be allowed to exceed that equivalent to 2–3 cc. of 0.1 *N* sodium hydroxide for 20 cc. of mash. After a period of 18 hours the contents of the seed tub is ready to be transferred to the main fermenters, where the acidity should be checked every 6 hours and where the acidity should not exceed 5 cc. of 0.1 *N* sodium hydroxide to 20 cc. of mash.

Twenty-four hours after the contents of the fermenters have been seeded from the seed tubs containing the mold, it is time to introduce the yeast. The contents of the fermenters are then cooled to 32° C. and seeded with a suitable yeast culture, which has been prepared in a pure condition in a suitable yeast-propagating apparatus, and developed to the requisite volume in a seed tub. The mash is aërated for about 6 hours after the introduction of the yeast, and the fermentation usually completed in 48 hours, the whole process being completed in 3 days. The third stage or alcoholic fermentation of the saccharified mash is in no sense different from any other industrial alcoholic fermentation of grain.

In the original Amylo process the saccharification and fermentation of the mash had to be carried out in special closed tanks to prevent the infection of the mash with bacteria and other microörganisms which might find the substrata suitable for their development. In more recent years there has been developed what is known as the Boulard process, in which a more vigorous and robust species of Mucor is used, known as Mucor Boulard No. 5. This species was isolated from grain in the Far East. It is characterized by its saccharifying power, and its ability to hold its own in competition with adventitious infection. Consequently it is claimed for the Boulard process that both the saccharification of the starch and the alcoholic fermentation of the sugar can be carred out in open vats, just as in the ordinary grain distillery. In the Boulard process a bub is prepared from the pure culture of the mold, which is about one-sixth the volume of the main mash. The bub or seed is propagated on sterile mash and in closed vessels, and, when ready, it is transferred to the main fermenters of the open type. Yeast and mold are added to the main mash in the Boulard process simultaneously, and the whole process is completed in 48 hours. Owing to the rapidity with which the fermentation proceeds, foreign organisms have but little opportunity to develop, and hence there is no necessity for the use of closed and costly fermenters in the process.

Under the original Amylo process, the time required for the completion of the fermentation was from 48 to 50 hours longer than the ordinary method. This was quite a drawback, and no doubt has been one of the contributing factors against the general adoption of the process in grain distilleries.

Advantages of the Process

The most important advantages in the processes using species of Mucors for the saccharification of starch are as follows: (1) economy due to saving in malt; (2) decreases in losses due to infection introduced with the malt; (3) increased yields of alcohol; and (4) higher purity of alcohol formed in the mash.

As from 10 to 15 per cent malt is used on an average on the weight of grain contained in the mash, the saving in the cost of malt is very considerable and certainly worth the effort. Nettleton calculated in 1913 that the saving in malt would make one gallon of 95 per cent alcohol cost $11^1/_4$ d. by the Amylo process, as against 1 s. $6^1/_2$ d. by the older British method. The general experience of the users of the Amylo process has been that their yields will average considerably higher than when using the malting process for saccharification. It is reported that the yields are about 10 per cent higher than in the old process, owing to a more complete saccharification of the starch.

In a study of the Boulard process in Madagascar by the Institut Colonial de Marseille, it was found that the yields of alcohol were from 37 to 39 liters of alcohol per 100 kg. of maize as against 34 liters by the malting process. The following data (*3*) give the comparative yields by the two processes:

Material *Kg.*	Raw Material	Starch Content *%*	Starch Consumed in Fermentation *%*	Yield from 100 kg. Grain 100 kg. Starch = 66 l. Wine Spirits *Liters*
		AMYLO PROCESS		
100	Maize	60	60	39.60
90	Maize	60	54–59.2	39.07
10	Barley unmalted	52	5.2	
		MALTING PROCESS		
90	Maize	60	54–58.0	38.28
10	Barley (as malt)	40	4.0	

Another advantage of the Amylo process over the old malting process is in the elimination of the barley and the substitution therefor of the corresponding amount of maize with its higher starch content. Other advantages of the process that are not generally known, and of which too little, perhaps, has appeared in the literature, are the high temperature at which the process can be efficiently carried out, and the relatively high percentage of fat contained in the residue from the stills. This residue is easily filterable, as the mycelia of the mold form a firm cake, and the product can be produced as cattle feed and has good keeping qualities. The cake contains 20 per cent of fat which can be recovered by extraction, and used for a variety of purposes.

Owing to the adaptability of the process to high temperatures (the optimum appearing to be from 35–38° C.), it should be in great demand in grain distilleries in all tropical and subtropical climates. A special yeast is used in conjunction with the Mucor species, *Saccharomyces anamensis*, isolated from a mixture of wild yeast found on sugar cane in Cochin China; in the Boulard process rapidly acting yeasts, known as yeast Boulard No. 21–30, are employed. Usually the concentration of the sugar in the mash is at its maximum (approximately 11.3 per cent) about 53 hours after the introduction of the mold, after which time it falls rapidly.

Still another advantage is the higher concentration of the mashes employed, and the corresponding saving in steam for distillation. In the Amylo process, the proportion of maize to mash is often as high as 18 to 22 kg. per 100 liters; on an average it is approximately 15. These mashes allow for a theoretical yield of 7.5 to 8.5 per cent by volume of spirits, and represent a concentration considerably higher than is usually obtained under the malting procedure.

Neither the amylo nor the Boulard process has been adopted in those countries like England where the excise laws require that the gravity of distiller's wort shall be determined before fermentation by the saccharimeter, which is impracticable in any process where the saccharification and the fermentation of the resulting sugar takes place simultaneously. It is quite obvious that the introduction of the more effective of the Mucor processes for grain distilleries in this country would enable them to reduce still farther the cost of their operation and enhance their opportunities for competing with some of the cheaper sources of industrial alcohol.

LITERATURE CITED

(1) Bonnefoy, M., "Fabrication de l'alcool par les procédés H. Boulard," pp. 169–81, Supplement tech. aux cahiers coloniaux de l'inst. colonial Marseille, 1931.

(2) Delemar, A., *Chimie & industrie*, 2, 892 (1919).

(3) Foth, G., "Handbuch der Spritusfabrikation," pp. 351–62, Paul Parey, Berlin, 1929.

(4) Société d'exploitation des procédés H. Boulard, "Procédés pour la fabrication des alcools industriels des alcools coloniaux et pour les industries bacteriologiques," pp. 1–8, 1931.

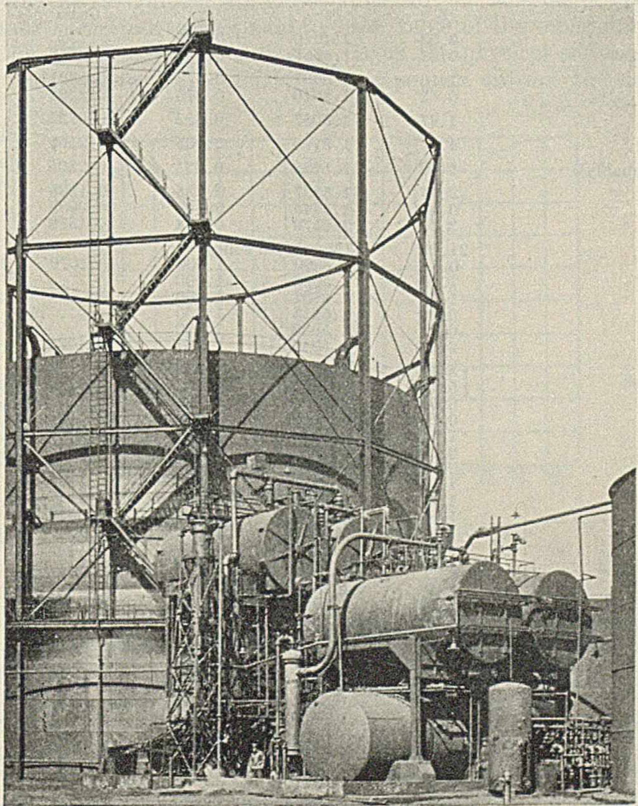
(5) Williams, M., "Power Alcohol," pp. 53–8, Oxford Tech. Press, 1922.

RECEIVED July 19, 1932.

Influence of Bunker Enriching Oil on Composition of Distillates from Water Gas Tar

CARROLL W. GRIFFIN, Rutgers University, New Brunswick, N. J.

RATHER recently the practice of using bunker oils for enriching water gas has been employed. In order to study the tar resulting from this practice, samples were taken from one of the New Jersey plants in which the enriching oil was a bunker C oil of the following specifications: viscosity (Saybolt Furol at 122° F., or 50° C.), maximum 300; sediment maximum, 0.25 per cent. This bunker oil had been obtained from grade B coastal oil of southeast Texas, reduced to a 16° to 17° A. P. I. gravity by the removal of light gasoline, gasoline and naphtha, kerosene distillate, furnace oil (light gas oil), and some lubricating oil. The plant uses the standard Lowe water gas sets and a 5-minute cycle of operation. During the up-run the bunker oil is sprayed directly on the hot coke in the generator and into the unpacked carburetor. About 14 gallons of tar are introduced into the generator during each back run. (A condensation from the gas occurs in various units of the plant and accumulates as a tar.) In the plant considerable amounts of tar had been distilled, the object being the production of a pitch melting at 68° to 75° C. (Kramer Sarnow, 0.5-inch cube in air). As a result of this distillation there had accumulated a quantity of oil, and this material was selected for study in order that its composition and properties might be determined as far as possible. This oil during the plant distillation is collected in two fractions, one of a specific gravity less than water and the other heavier than water. The oils amounted to 23 per cent of the weight of the tar. About seven-tenths of the distillate from the tar was represented by the lighter and more volatile oil.



STEAM STILLS

PRELIMINARY TREATMENT AND FRACTIONATION OF LIGHTER OIL

The oil as obtained from the plant contained very little water, and was distinctly murky. A small amount of sediment was present, probably material mechanically carried over during the plant distillation. In order to remove this material and bring about a rough fractionation, the oil was distilled in Pyrex flasks of 3 liter capacity without the use of columns of any kind. Four fractions were collected: up to 216° C., 216–235°, 235–270°, and 270–300°. A small tarry residue remained in the flask at 300°. After a week a white solid crystallized out from the 216–235° portion, and more of the solid was then removed by cooling this oil to −19° C. and filtering with a suction filter at room temperature. This solid was later proved to be naphthalene.

The oils were next washed three times with a 20 per cent solution of sodium hydroxide, and then three times with a 20 per cent solution of sulfuric acid.

The tar acids or phenolic substances removed represented 0.2 per cent by volume of the oil, and the tar bases amounted to 0.5 per cent.

The four portions of the oil were next fractionated, using a 30-inch (76.2-cm.) Snyder column (*12*) made of Pyrex glass, containing fourteen balls. The column was wrapped with sheet asbestos and resistance wire and then with asbestos cord. At higher distillation temperatures it was necessary to apply heat through the resistance wire to the column in order to prevent an overflow of liquid oil into the side arm. Always, however, the smallest heating possible was applied to the column itself.

TABLE I. BOILING RANGE OF TYPICAL CUTS

239–241° C. Cut[a]		265–267° C. Cut[a]		355–365° C. Cut[b]	
Temp.	Vol. distd.	Temp.	Vol. distd.	Temp.	Vol. distd.
° C.	*Cc.*	*° C.*	*Cc.*	*° C.*	*Cc.*
234	1 drop	261	1 drop	348	1 drop
236	5	263	5	351	5
237	10	264	10	354	10
238	15	264.5	15	355	20
239	25	265.5	25	356	30
240	35	267	35	356.5	40
241	40	268	40	357.5	50
243	45	270	45	358	60
				359	70
				260.5	80
				363	90
				367	95

[a] From light oil; 50 cc. used.
[b] From heavy oil; 100 cc. used.

Fractionation was carried out three times, using fourteen ball columns sealed to a liter flask for the first treatment and to a 500-cc. flask for the last two treatments. A very slow rate of distillation was maintained. Cuts were made at 10° intervals except between 225° and 285° C. where 2° cuts were taken. Table I gives the boiling range of three typical cuts after the last fractionation and indicates the efficiency of the column. (The third set of data is for the heavy oil.)

Very little oil distilled below 125° C. so that the first cut was made at that point. A small quantity was obtained as high as 335° C. Table II gives, among other data, the percentage yield for the various cuts. In Figure 1 the distillation curve is plotted. Several noticeable points occur in this curve. They are approximately at 140°, 160–180°, 215°, 238–242°, 262°, and 268° C. These, roughly, are the boiling points of the xylenes, the trimethylbenzenes, naphthalene, the methylnaphthalenes, and the dimethylnaphthalenes.

GENERAL CHARACTERISTICS OF DISTILLATES

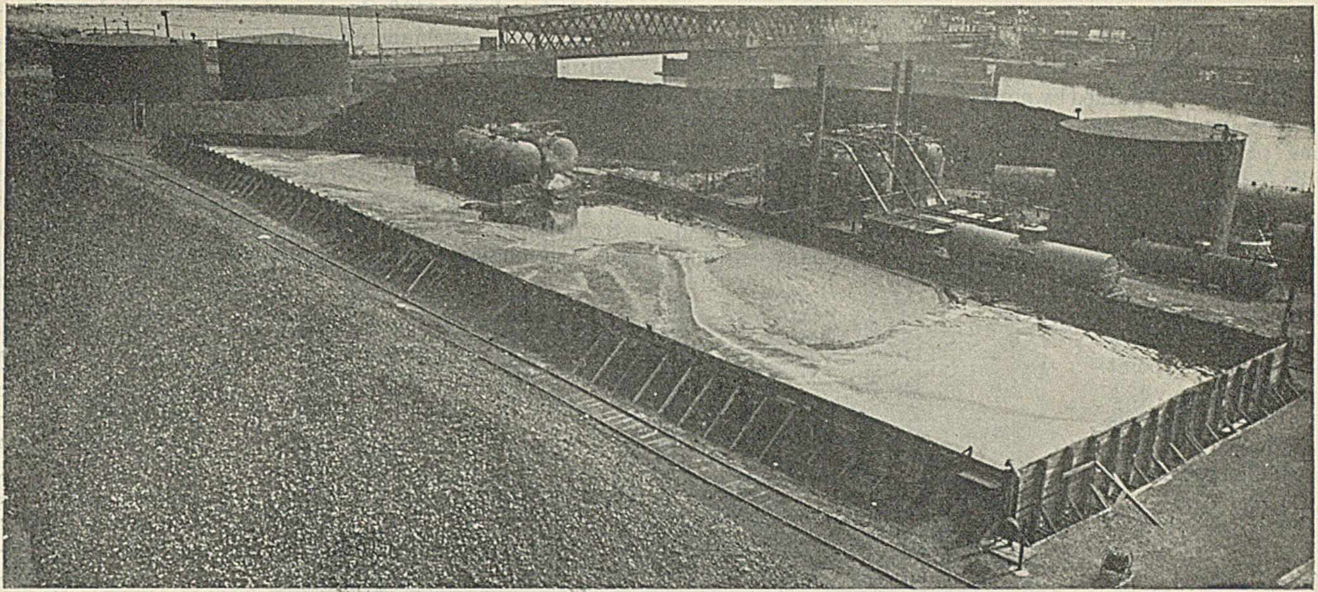
COLOR AND ODOR. The color of these oils from 125° to 155° C. was water-white even after months of standing. Those from 155° to 235° C. merged in color from faint yellow to deep amber, and all became somewhat darker on standing. The oils boiling around 240° C. were found to be distinctly blue, and at about 255° C. they were light green. Thereafter yellow became the predominating color which continued with gradual deepening in color for all higher-boiling oils.

Concerning odor, the oils in the 125–175° C. range were distinctly aromatic, indicating the presence of simple methyl derivatives of benzene. Those boiling above 175° C. were found to possess an odor similar to that of manufactured gas.

INDICES OF REFRACTIONATION AND SPECIFIC GRAVITIES. The refractive index and the specific gravity of the oils were determined and are given in Table II. The portion of oil

TABLE II. YIELDS AND PROPERTIES OF LIGHT OIL AND PARAFFINS THEREIN

Distg. Temp. of Oil	Chief Component	Yield by Vol.	Refractive Index at 22° C.	Sp. Gr. at 22° C.	Bromine Absorbed per cc.	Vol. of Paraffins in Respective Cuts	Refractive Index of Paraffins at 22° C.	Sp. Gr. of Paraffins at 22° C.
° C.		%			*Gram*	%		
Up to 125	Toluene	0.63	1.4910	0.865	....	...	....	....
125–135		0.41	1.4957	0.870	0.1513	...	....	....
135–145	Xylenes	1.16	1.5007	0.872	0.1801	...	....	....
145–155		0.52	1.5010	0.876	0.2298	Zero	....	....
155–165	Mesitylene	1.47	1.5057	0.885	0.0723	...	....	....
165–175	Pseudocumene	4.07	1.5175	0.905	0.2569	...	....	....
175–185	Hemimellitene (probably)	5.02	1.5288	0.925	0.2805	Zero	....	....
185–195		2.31	1.5337	0.935	0.1288	Zero	....	....
195–205		0.63	1.5445	0.947	0.0933	3.0	1.4597	0.8371
205–215		3.56	1.5579	0.964	0.1318	...	....	....
215–225	Naphthalene	21.26	(Nearly all solid)			...	....	....
225–227		0.14	1.5890	1.000	0.1070	...	....	....
227–229		1.20	1.5895	1.000	....	...	....	....
229–231		1.36	1.5901	1.000	....	...	....	....
231–233		0.66	1.5914	1.000	....	...	....	....
233–235		0.76	1.5938	1.000	....	...	....	....
235–237		2.21	1.5940	1.001	0.1021	2.8	....	....
237–239	Methylnaphthalenes	3.48	1.5942	1.002	....	2.8	1.4608	0.8470
239–241		5.18	1.5950	1.002	....	...	....	....
241–243		5.01	1.5950	1.002	....	2.8	1.4640	0.8476
243–245		0.68	1.5948	1.002	....	...	....	....
245–247		1.46	1.5940	1.002	0.0848	2.8	....	....
247–249		0.33	1.5930	1.001	....	...	....	....
249–251		0.57	1.5922	1.000	....	...	....	....
251–253		1.86	1.5916	1.000	....	...	....	....
253–255		1.94	1.5918	1.000	....	2.8	....	....
255–257		1.89	1.5909	1.000	0.0570	...	....	....
257–259		1.98	1.5909	1.000	....	3.2	....	....
259–261		1.98	1.5903	1.000	....	...	....	....
261–263		4.94	1.5907	1.000	....	3.4	1.4602	0.8446
263–265	Dimethylnaphthalenes	1.48	1.5903	1.000	....	...	....	....
265–267		1.49	1.5901	1.001	0.0407	4.0	1.4622	0.8476
267–269		3.57	1.5893	1.001	....	3.8	1.4631	0.8483
269–271		1.09	1.5891	1.002	....	5.0	....	....
271–273		0.64	1.5887	1.001	....	...	....	....
273–275		1.08	1.5877	1.001	....	4.6	....	....
275–277		0.85	1.5871	1.001	0.0291	...	....	....
277–279		0.36	1.5860	1.001	....	4.6	....	....
279–281		0.36	1.5859	1.001	....	4.5	1.4632	0.8493
281–283		0.24	1.5854	1.001	....	...	....	....
283–285		0.56	1.5855	1.001	0.0291	5.8	....	....
285–295		2.30	1.5885	1.006	....	5.8	....	....
295–305		2.13	1.5920	1.015	0.0291	...	....	....
305–315		2.15	1.5990	1.028	....	...	....	....
315–325	Anthracene and phenanthrene	2.07	(All	...	....	...	....	....
325–335		0.96	solid)	...	....	...	....	....



Pitch Bay and Cooling Tanks; Side and Rear View of Direct Fired Stills

boiling below 125° C. was redistilled and a drop taken when the thermometer registered 111°. This gave a refractive index at 22° C. of 1.4920, a fair check on the presence of toluene. The refractive index for the oil in the xylene range is very close to the values given by International Critical Tables for *o*-, *m*-, and *p*-xylenes. The refractive index obtained for oils boiling from 160° to 175° C. is a little higher than that of the pure trimethylbenzenes, and fairly good checks are found for methyl- and dimethylnaphthalenes. In the last two cases the index is undoubtedly affected by the presence of paraffins, which lowers the constant (*14*).

In general, the specific gravities as determined are close to the values of those compounds suspected to be present. This property is also affected by paraffins. It is unlikely that indene ($C_6H_4CHCHCH_2$) and styrene ($C_6H_5CHCH_2$), which are doubtless present in small quantities, could affect the physical constants of the oil very much. Brown and Howard (*3*) report approximately one per cent of these compounds in samples of water gas tar investigated by them. Anhydrous stannic chloride, which polymerizes styrene, was added to the 145–155° C. portion of the oil of the present study, and roughly one per cent was precipitated. A slight precipitation also resulted when this reagent was added to the 185–195° C. portion. This range includes the point at which indene boils.

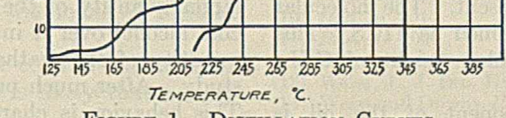


Figure 1. Distillation Curves

1. Light oil 2. Heavy oil

Absorption of Bromine. As a measure of unsaturated hydrocarbons, several samples were treated with bromine. This was done by titrating the oils with a solution of bromine in carbon tetrachloride (0.1346 gram of bromine per cc.). To reduce substitution reactions to a minimum, the titrations were carried out at −10° to −18° C. and kept in the dark except for a momentary exposure to light in obtaining the end point. Following the method of Brown (*2*) the end point was taken when the natural color of a slight excess of bromine persisted at least 3 minutes. After reaction the hydrobromic acid formed (always a small quantity) was determined and the bromine actually reacting additively computed. Table II gives these results.

Paraffins. Table II gives the data on paraffins found present in the oils. The method employed for determining paraffins was that of Weiss (*13*). Molecular weight determinations by the freezing point method were made on three of the paraffins. The one boiling at 237–239° C. gave a molecular weight of 197.8 which is close to that of the compound $C_{14}H_{30}$; for the paraffin boiling at 265–267° C. a molecular weight of 229 was obtained; and for that boiling at 279–281° C., a value of 228.2. Each of the last two is near the value of the molecular weight of the compound $C_{16}H_{34}$. From the physical constants obtained it appears that these compounds are not the normal saturated hydrocarbons of the methane series but largely either branched-chain isomers of the normal molecules, or else naphthenes, since the latter are characterized by lower boiling points and higher densities than the normal paraffins containing the same number of carbon atoms.

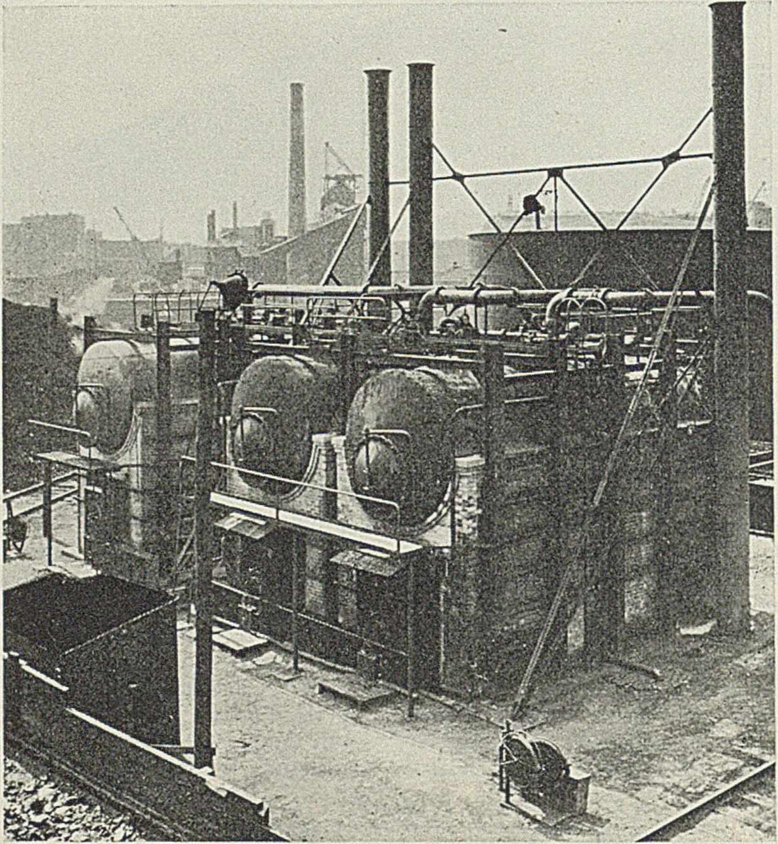
In addition to the measurements already outlined, further study was made of those cuts which give abrupt rises in the curve of Figure 1 to identify, if possible, the chief component in the several cases. A brief description of the identifications made follows.

Toluene. The portion boiling below 125° C. was distilled again after the third fractionation and a small portion cut at 111° C. This sample was nitrated (*11*). 2,4-Dinitrotoluene (melting point, 70–71° C.) was obtained and its melting point determined as 69° C. After five crystallizations the melting point was found to be 70° C.

Xylenes. The first distinct maximum in curve 1 of Figure 1 appears at about 140° C. The 10° cut at 135–145° C. was examined for xylenes by Levinstein's method (*6*) with the following results:

	%
m-Xylene, approximately	70
p-Xylene, approximately	30
o-Xylene	Trace

m-Xylene was identified by preparing from this cut, trinitro-*m*-xylene (melting point, 181–181.5° C.) which gave a melting point of 181.5° C. Trinitro-*p*-xylene (melting point, 138.5–139° C.) was prepared. It melted at 139.5° C. Levinstein's method of preparing *o*-xylene yielded a few crystals of the sodium *o*-xylene sulfonate which by treatment with sulfuric acid formed a scum of oil, presumably *o*-xylene. A molecular weight determination on the mixed xylenes by the freezing point method gave a value of 106.5 as compared with the formula weight of 106.12.



FRONT AND SIDE VIEW OF DIRECT FIRED STILLS

TRIMETHYLBENZENES. The next irregularity in the distillation curve occurs around 170° to 180° C. which suggests the presence of the trimethylbenzenes. It was not possible to form the trinitro-compounds of sharp melting points without distilling and taking a few drops at the exact boiling points of mesitylene and of pseudocumene. When this was done, trinitromesitylene (melting point, 235° C.) was prepared from the sample so obtained, and it melted fairly sharply at 236° C. Trinitropseudocumene (melting point, 184° C.) was prepared and found to melt slowly at 181–184° C. Jacobsen's method (*5*) was used to obtain a separation of mesitylene and pseudocumene in the oil, and the sulfonyl chloride of the latter was prepared. Its melting point (61° C.) was found to be 59–60° C. From the shape of the distillation curve it is believed that hemimellitene which boils at 175° C. was probably present. The molecular weight for this cut of oil was determined as 119.8. This agrees closely with the actual molecular weight of $C_6H_3(CH_3)_3$—namely, 120.14.

NAPHTHALENE. The largest component of the oil is naphthalene. This composes nearly 19 per cent of the lighter oil, this quantity being obtained by originally freezing out as much as possible, followed by repeated fractionation. A pure sample was prepared by crystallization from alcoholic solution which gave a melting point of 80.5° C. The picric acid compound of naphthalene (melting point, 150.5° C.) was prepared (*10*) and found to melt at 150.5° C.

METHYLNAPHTHALENES. These compounds boil around 240° C. No attempt was made to identify the isomers. The picric acid derivative was prepared from alcoholic solution of the oil from the 238–240° C. cut. The melting points of these picrates are 115° and 116° C. The sample prepared melted sharply at 116° C. A molecular weight determination gave 143.7 as compared to the formula weight of 142.14.

DIMETHYLNAPHTHALENES. Two prominent points in the distillation curve are found around 261–263° C. and 267–269° C. This would suggest the presence of α- and of β-dimethylnaphthalenes; the former is said to boil at 263° and the latter at 266° C. The picric acid derivatives were prepared from the oils in these distillation ranges, and they were found to melt at 118.5° and at 120° C. Mulliken (*9*) gives the melting point of α-dimethylnaphthalene picrate as 139° C. Beilstein (*1*) gives six different melting points for the picric acid compounds of the dimethylnaphthalenes, ranging from 118° to 180° C. Beilstein gives this picrate from coal tar as melting at 118–119° C. The molecular weight of the oils of this range was found to be 157.4, as compared to 156.16 for dimethylnaphthalene.

ANTHRACENE AND PHENANTHRENE. During fractionation a solid condensed from the distillate coming over at 315° up to 335° C. The crude possessed a yellow color and, upon recrystallization from several solvents, became more nearly white. This was treated with chromic acid and glacial acetic acid, and the anthraquinone so formed was identified by repeatedly obtaining and destroying the red color resulting on treatment with sodium hydroxide solution and zinc. The solid thus contained anthracene. It was noticed that, in filtering after a recrystallization of the anthracene, a white fluffy growth of crystals took place in the filtrate, which had a melting point of 93° C. Starting with a larger quantity of the yellow solid, and by slowly dripping cold alcohol over it in a filter paper and funnel, a sufficient quantity of the feathery crystals was obtained for further study. After much purifying it was found to melt at 95° C. This behavior is characteristic of phenanthrene (*7*). The picrate (melting point, 143° C.) was formed. It melted at 143° C. A molecular weight determination gave a value of 178.3. The molecular weight of phenanthrene is 178.15.

HEAVY OIL

The preliminary treatment and the fractionation of the oil which, as it comes from the fire stills of the plant, has a specific gravity greater than that of water, was similar to that already described for the lighter oil. A volume of 5000 cc. was taken for the study.

The soda and acid washes showed the presence of 0.41 per cent by volume of tar acids and 0.38 per cent of tar bases.

TABLE III. YIELDS AND PROPERTIES OF HEAVY OIL AND PARAFFINS THEREIN

DISTG. TEMP. OF OIL	CHIEF COMPONENT	YIELD BY VOL.	REFRACTIVE INDEX AT 22° C.	SP. GR. 22° C.	BROMINE ABSORBED PER CC.	VOL. OF PARAFFINS IN RESPECTIVE CUTS	REFRACTIVE INDEX OF PARAFFINS AT 22° C.	SP. GR. OF PARAFFINS AT 22° C.
° *C.*		%			*Gram*	%		
Up to 215		2.56	....	...	....	...	....	....
215–225		5.37	....	...	....	...	....	....
225–235		1.21	1.5880	1.000	0.1045	2.9	1.4606	0.8466
235–245	Methylnaphthalene	8.58	1.5970	1.000	0.0905	2.8	1.4638	0.8475
245–255		5.16	1.5980	1.002	0.0652	2.8	1.4635	0.8450
255–265	Dimethylnaphthalene	12.67	1.5981	1.004	0.0441	3.3	1.4631	0.8470
265–275		11.46	1.5987	1.008	0.0361	3.9	1.4640	0.8491
275–285		5.29	1.5988	1.009	0.0285	5.2	1.4646	0.8495
285–295		5.01	1.6003	1.016	0.0287	5.5	1.4651	0.8496
295–305		4.05	1.6052	1.027	0.0281	5.7	1.4660	0.8505
305–315		4.43	1.6129	1.035	0.0209	2.4	1.4710	0.8515
315–325	Anthracene and phenanthrene	3.04	1.6200	1.046	0.0181	3.2	1.4714	0.8570
325–335		8.73	1.6291	1.056	0.0171	3.2	1.4733	0.8590
335–345		9.11	1.6409	1.069	0.0151	3.2	1.4725	0.8603
345–355		4.80	1.6513	1.077	0.0151	4.2	1.4722	0.8683
355–365		2.70	1.6550	1.080	0.0132	4.2	1.4759	0.8767
365–375		2.52	1.6614	1.088	0.0132	4.2	1.4765	0.8767
375–385		2.02	1.6710	1.104	0.0132	2.4	1.4801	0.8770
385–410	Methylanthracene	1.29	....	...	....	...	....	....

Cuts of 10° C. were made during the fractionation; the third set of data of Table I is typical of the boiling ranges of these cuts. Distillation began at 180° C. and the temperature rose rapidly to 205°. The first cut was therefore made at 215°. The flask became dry at 410°. Between 385° and 410° a yellow solid distilled over so that the last cut was made including this 25° interval. The cuts obtained up to 325° C. yielded oils practically identical in properties with oils of corresponding ranges from the lighter oil. Table III lists these properties.

The last component obtained from the lighter oil was a mixture of anthracene and phenanthrene. These substances were found to distil from the heavy oil between 315° and 345° and most abundantly from 335° to 345° C. The quantity of these compounds amounted to 7.70 per cent by weight of the heavy oil and 1.06 per cent by weight of the light oil. The Höchste method (*8*) was used to determine the quantity of pure anthracene. The result showed the presence of pure anthracene to an extent of 30.20 per cent by weight. Using this figure, and knowing that plant distillation of the tar yields oil equal to about 23 per cent of the weight of the tar and in the ratio of 16 to 7 for the light oil and the heavy oil, the following figures are obtained for pure anthracene: in the heavy oil, 2.32 per cent; in the light oil, 0.32 per cent; in the total oil, 0.93 per cent; and on the basis of tar, 0.21 per cent.

The solid material distilling at 385–410° C. possessed a brilliant yellow color with the faintest tinge of green. It was found to be only slightly soluble in alcohol and ether; soluble in benzene, chloroform, and carbon disulfide. After crystallizing from chloroform, it was found to have a melting point of 204° C. These facts indicated that the substance was probably methylanthracene. Confirmation of this compound was obtained by oxidation to methylanthraquinone (*4*), melting point 163–167° C., which was found to melt at 167–168° C.

Because of the faint greenish yellow color of the material distilling in the 385–410° C. range, it is likely that a trace of chrysogen was present.

Table IV gives the yield of some of the chief components of the oils based, first, on the total oil as obtained from the tar—that is, computed on the basis of the light oil plus the heavy oil; secondly, based on the tar.

TABLE IV. YIELDS OF CHIEF CUTS BASED ON TOTAL OIL AND ON TAR

DISTG. TEMP. OF OIL	CHIEF COMPONENT IDENTIFIED	YIELD BY WEIGHT	
		Based on total oil[a]	Based on tar
° *C.*		%	%
Up to 125	Toluene	0.44	0.10
135–145	Xylene	0.81	0.17
155–165	Mesitylene	1.02	0.23
165–175	Pseudocumene	2.83	0.65
	Naphthalene	14.64	3.37
235–245	Methylnaphthalene	14.13	3.25
255–265	Dimethylnaphthalene	12.39	2.85
265–275	Dimethylnaphthalene	8.88	2.04
	Anthracene and phenanthrene	3.08	0.71
385–410	Methylanthracene	0.40	0.09

[a] Light and heavy.

ACKNOWLEDGMENT

The writer desires to express his thanks to the New Jersey Gas Association which sponsored this investigation and to W. T. Read, P. A. van der Meulen, and D. L. Cottle, all of the School of Chemistry of Rutgers University, whose advice was frequently sought and generously given.

LITERATURE CITED

(1) Beilstein, Handbuch der organischen Chemie, 4th ed., Vol. IV, p. 271, Springer, 1918.
(2) Brown, IND. ENG. CHEM., 20, 1179 (1928).
(3) Brown and Howard, *Ibid.*, 15, 1147 (1923).
(4) Fischer, *Ber.*, 8, 675 (1875).
(5) Jacobsen, *Ibid.*, 9, 256 (1876).
(6) Levinstein, *J. Soc. Chem. Ind.*, 3, 77, 354 (1884).
(7) Lunge, "Coal Tar and Ammonia," 5th ed., Part I, p. 257, Van Nostrand, 1916.
(8) *Ibid.*, Part III, p. 634.
(9) Mulliken, "Identification of Pure Organic Compounds," 1st ed., Vol. I, p. 193, Wiley, 1904.
(10) *Ibid.*, p. 201.
(11) *Ibid.*, p. 202.
(12) Simons and Wagner, *J. Chem. Education*, 9, 127 (1932).
(13) Weiss, J., J. IND. ENG. CHEM., 10, 1009 (1918).
(14) Weiss and Downs, *Ibid.*, 15, 1022 (1923).

RECEIVED August 4, 1932. The author's present address is Vassar College, Poughkeepsie, N. Y.

VIOLIN MADE FROM ORTHOPEDIC PAPER HAS GOOD TONE. A violin constructed from orthopedic gummed paper and reported to have a tonal softness comparable to instruments fashioned from selected woods by some of the better-known Italian craftsmen was recently shown in Vienna, Austria, according to a report to the Department of Commerce.

The acoustic properties of the paper were accidentally discovered during the process of manufacturing orthopedic appliances and the violin was constructed as an experiment. The report to the department does not state whether the experiment will be conducted beyond the construction of the one violin.

While it is quite possible to easily construct from paper an instrument rigid enough to permit the use of a violin sounding board the purity and richness of the musical notes to be had therefrom cannot be evaluated in advance of a test, according to Paul Heyl, Bureau of Standards, Department of Commerce.

Water Content of Certain Fire-Protective Media

M. G. Mellon and J. E. Heck, Purdue University, Lafayette, Ind.

For insulating certain containers against fires, various materials such as natural cement, mixtures of natural and Portland cement, and plaster of Paris (gypsum) may be used, either with or without admixtures of other materials such as Sil-O-Cel, Zonolite, or kieselguhr. In preparing the mixtures which set when put in place, considerable water is added to the other ingredients before the material is poured.

According to certain manufacturers, particularly makers of fireproof safes, the protection afforded for a short time against high temperatures depends, to a considerable degree, upon the amount of water retained initially by the medium. This assumption is based on the belief that, in case of fire, more or less heat is absorbed (*3*) by the insulating medium in dehydrating such constituents as gypsum and in evaporating the water. Therefore, other things being equal, the more water to be dissociated and evaporated, the longer will be the period of protection. Presumably different combinations might retain the same amount of water but lose it at different temperatures, or possibly even at different rates at the same temperature. Also the presence of a highly humidified atmosphere within a safe is said to minimize the development of weakness and lifelessness of paper within the safe on exposure to elevated temperatures.

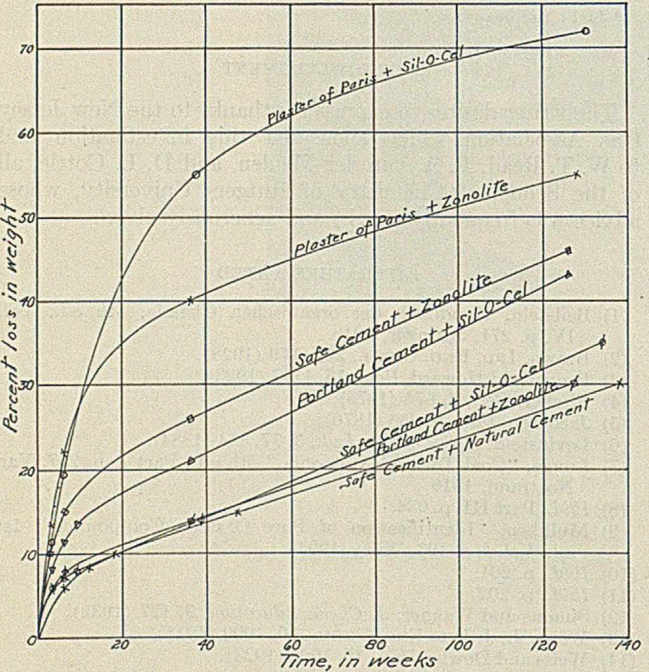


Figure 1. Curves Showing Loss of Weight for Different Fire-Protective Media

However, the ultimate value of an insulating medium probably depends largely upon its properties as a conductor of heat, the better conductor being the less desirable insulator; but it also seems probable that no one characteristic, such as the content of water, can be used as the only criterion in judging the value of a given medium for insulating purposes. Since various combinations used do contain enough water for the material to be poured, it seemed of interest, as part of a broader study, to determine the rate at which the water was lost and also the amount retained by the dried material.

Experimental Procedure

The plaster of Paris used was the ordinary commercial material. There were three cements: a special cement, manufactured for filling fireproof safes; a natural cement; and a high-grade Portland cement. Where the above mentioned materials were used only as binders, two fillers were tried: Sil-O-Cel (*2*), a siliceous material prepared from celite; and Zonolite (*1*), a product prepared by thermal exfoliation of a micaceous mineral found in Montana.

Table I. Composition of Fire-Protective Media

Curve	Dry Material Name	Dry Material Amount	Water Grams	Loss on Ignition %
1	Safe cement + natural cement	1:1 (by weight) 635 grams	378	25.9
2	Safe cement + Sil-O-Cel	25:8 (by weight) 400 grams	400	42
3	Portland cement + Sil-O-Cel	5:1 (by vol.) 126 + 139 grams	435	40
4	Plaster of Paris + Sil-O-Cel	3:1 (by vol.) 126 + 139 grams	450	41.4
5	Safe cement + Zonolite	2:3 (by vol.) 278 + 82 grams	310	27.2
6	Portland cement + Zonolite	2:3 (by vol.) 278 + 58 grams	250	27
7	Plaster of Paris + Zonolite	13:4 (by weight) 385 grains	374	35.7

The different combinations tried were mixed and placed in test tubes 8 × 1 inch (20.3 × 2.5 cm.), constricted about 1 inch from the upper end to a diameter of about 0.5 inch (1.3 cm.), enough material being used to reach just above the constriction. In order to permit evaporation, a piece of cardboard was fitted in the mouth of the tube and pushed down to the solidified mass. The loss of weight was determined at various intervals, at least 2.5 years elapsing between the time of preparing the tubes and the last weighing. Three years after preparation, the tubes were broken and the loss on ignition determined by igniting, at about 1000° C., a sample taken midway between the constriction and the lower end of the tube.

The data in Table I show the different combinations used, together with the proportions in which the materials were mixed. In all cases three tubes were made for each mixture, the data recorded being an average for the three. Each given combination, such as those indicated in Table I, was mixed with different amounts of water, including amounts both above and below those known to be employed in certain cases commercially. The amounts indicated in Table I were sufficient to permit fairly easy mixing. For this condition some combinations, such as those containing Sil-O-Cel or plaster of Paris, required much more water than others.

Discussion of Results

The curves in Figure 1 show typical results for loss of weight on standing. The amount of water indicated in Table I as having been used for each of the combinations for which curves are given is approximately the mean of the extremes used. In all cases the loss of weight was directly proportional to the amount of water used. In Table I is shown also the loss on ignition. The slowness with which the samples containing plaster of Paris came to constant weight was taken to indicate some decomposition of calcium sulfate to the oxide. It is of interest to note that a previous worker in this laboratory obtained a loss on ignition of 22.5 per cent on a sample having the composition represented by curve 1, which had been in a safe 18 years. There was no apparent shrinkage in the volume of the specimens which had been in the tubes 3 years.

Although some of the mixtures studied have been used in filling the steel shells of fireproof safes, it seems probable, because of the different conditions prevailing, that the results obtained cannot be considered as indicating closely how such insulators attain atmospheric equilibrium in a safe. The data presented seem to justify the following statements as legitimate conclusions to be drawn from this work:

1. There was a relatively large loss of weight in all cases over a period exceeding 2.5 years.
2. The percentage loss was distinctly different for the different combinations, being largest in the combination containing Sil-O-Cel.
3. The continued upward trend of the curves indicates a probable further loss of weight.
4. The loss on ignition was different for the different combinations, but in no case was it as low as that obtained for a sample taken from a safe 18 years old.

Literature Cited

(1) Alley, *Eng. Mining J. Press*, 120, 872 (1925).
(2) Anonymous, *Chem. & Met. Eng.*, 31, 972 (1924).
(3) Hull, Bur. Standards, *Tech. Paper* 130, 4, 20 (1919).

Received June 15, 1932.

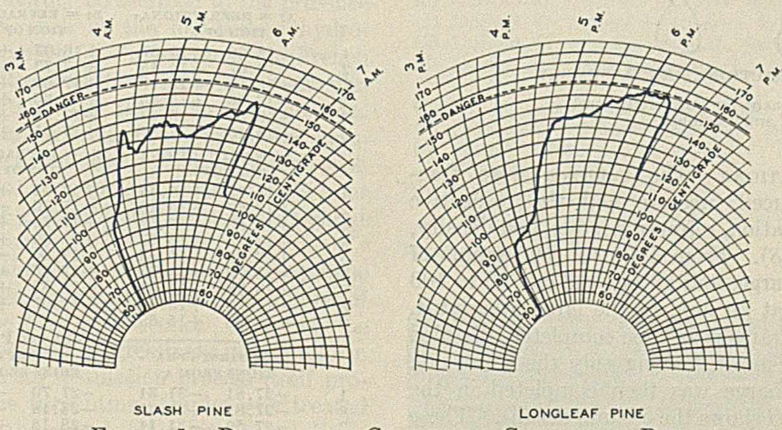
Component Distribution Trend in Commercial Turpentine Still Operation

S. Palkin, Industrial Farm Products Division, Bureau of Chemistry and Soils, Washington, D. C.

In processes such as the manufacture of synthetic camphor, terpin hydrate, and α-terpineol, preliminary fractionation of the turpentine (the initial material) has often been found advantageous (*1*, *4*). Not only may the effect of the "tailings" constituents be thus minimized, but fractions of higher β-pinene concentration may also serve more advantageously in certain special processes (*2*) in which this terpene is the active component.

A portion of the tailings mixture may be regarded as arising through oxidation, polymerization, etc., of the turpentine, and probably also through frothing and spattering of the rosin during distilling. The major portion in fresh turpentine, however, occurs originally in the gum and includes the aromatic derivatives which contribute the agreeable characteristic odor to gum turpentine.

Centralized plants, well equipped with fractionating towers, etc., are generally available in industries where turpentine constitutes a by-product, as in the manufacture of paper pulp or where it is one of a number of major products, such as in steam and solvent extraction or destructive distillation of pine and other woods. In these the turpentines represent arbitrarily set cuts in the distillation.



SLASH PINE LONGLEAF PINE

Figure 1. Distillation Charts for Commercial Runs

Gum turpentining, however, is carried out by a large number of producers directly in the field, in the main with simple fire stills under conditions where the use of elaborate engineering equipment is economically impracticable. These stills are generally quite large, about 10 feet in height (to top of neck), and 8 feet across. They have a capacity of about 10 barrels of gum per charge (about 51 gallons per barrel).

It is not unreasonable to assume, in view of the large size of the field distillation apparatus, that rectification takes place to a limited extent, tending to concentrate the tailings and also the β-pinene toward the end of the run.

A study of component distribution of commercial field-turpentine distillation under normal conditions was therefore undertaken to determine to what extent rectification takes place and to obtain data for ascertaining the practicability of dividing the product of distillation into several parts, each of which may serve as a better raw material for certain purposes than the whole turpentine. Since this procedure can probably be followed without change in field equipment and since it requires little or no extra labor, it may have some economic advantages.

Examination of two commercial runs in this investigation has demonstrated that, although rectification occurs to a limited degree, nevertheless a turpentine of higher pinene and lower tailings content than that of the whole turpentine is procurable by taking early cuts at appropriate points in the distillation.

Experimental Procedure

As the two species *Pinus palustris* (long-leaf pine) and *Pinus caribaea* M. (slash pine) constitute the sources from which practically all American gum spirits of turpentine are obtained commercially (*9*), two sets of authentic samples, representing these sources, were taken from runs made in a commercial still. Each set comprised three samples representative of the three cuts of the distillate. Sample 1 consisted of 51 gallons taken after the first 5 gallons at the beginning of the distillation had been run into a separate container; sample 2 represents the following 51 gallons; and sample 3 the last 18 gallons (long-leaf only).

The gum of each charge was mixed as well as the limited facilities permitted. As there is no provision in the field stills for running total reflux, it was thought that postponement of sampling until after the first 5 gallons of distillate came over might allow sufficient time for the steam agitation to effect a thorough mixing of the large charges of gum involved. This, however, was not entirely accomplished as will be seen later. Distillation charts for the respective runs are shown in Figure 1.

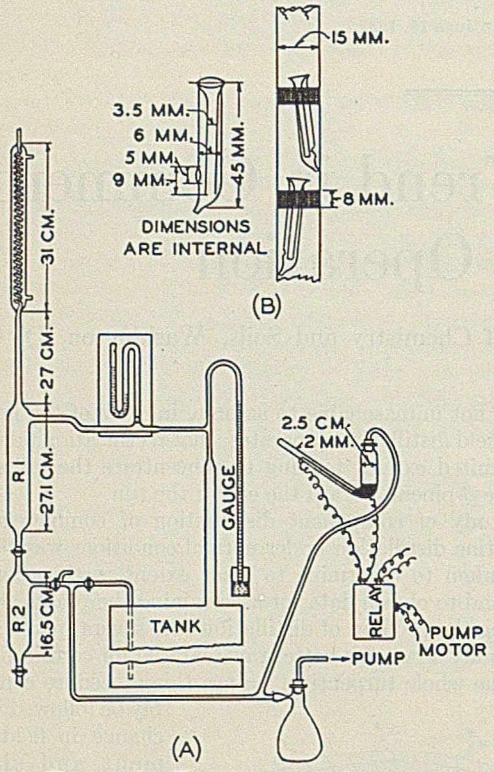


FIGURE 2. FRACTIONATING ASSEMBLY

A. Arrangement for pressure control
B. Detail of small column

LABORATORY DISTILLATIONS. The samples were fractionally distilled at reduced pressure and the respective fractions examined for rotation, refractive index, and density, as described previously (*8*). From 1000 to 1500 grams of sample constituted the charge, and all but the last 50 to 100 grams were fractionated at 20 mm. in the large apparatus. The remaining 50 to 100 grams were then completely distilled at lower pressure (3 or 4 mm.), leaving only the rosin, etc.

Fractionation of the charge was then completed in the small apparatus (Figure 2*B* shows the column detail). These fractions were also examined for rotation, refractive index, etc.

For purposes of calculation and to provide more accurate optical data on the tailings constituents, these fractions were refractionated. The respective proportions of α- and β-pinene and tailings were then determined by the optical method of Darmois and Dupont (*10*) as described previously (*8*).

EQUIPMENT. The fractionating apparatus used comprised the following: large fractionating assembly with a wire-gauze plate rectifying column (thirty-two plates, 5 cm. inside diameter, 200 cm. in height), which is an improved form of this type of column described earlier (*7*). The rest of the assembly, with the exception of the pressure control system and modifications of the thermal insulation, is similar to that described previously (*8*).

Pressure in the system was maintained constant by means of a short inclined mercury regulator and relay, shown in Figure 2*A*. Virtually all the distillations were carried out at 20 mm. or less. The short manometer regulator was found to be very effective for the purpose, both on account of the low resistance to mercury movement and increased sensitivity resulting from inclination of the contact arm.

Figure 2*A* also shows the relationship of the pressure control system to the column assembly proper. This assembly was in its general plan, including the plate column (twenty plates and about 120 cc. in height), like the large one. In view of the absence in the literature of mention of microplate columns suitable for fractionation in vacuum—that is, with low holdup and of sufficiently large capacity to handle comparatively large volumes of vapors incident to low-pressure operation—detailed measurements of this column are given (Figure 2*B*). The trap tubes contained only 0.3 cc. of liquid each, when primed.

Optical rotation measurements were made in the yellow (578 mμ) and in the green (546 mμ) by means of a Schmidt and Hansch polarimeter equipped with a spectroscope. Rotatory dispersion values so obtained are of particularly diagnostic significance (*10*).

After complete fractionation of each of the samples examined, the top three or four fractions (representing the highest concentration of α-pinene in each case) were further purified by refractionation. (Constancy of rotation for this terpene from each of the respective samples was attained practically after one refractionation, as shown in Table I.)

TABLE I. ROTATION DATA ON α-PINENE COMPONENTS OF TURPENTINE SAMPLES[a]

(Observed rotation in 10-cm. tube, in degrees)

SAMPLE	LONG-LEAF PINE					
	Yellow[b]	Green[c]	Yellow	Green	Yellow	Green
	A_1 = FIRST 4 FRACTIONS FROM A		B_1 = FIRST 3 FRACTIONS FROM B		C_1 = FIRST 4 FRACTIONS FROM C	
1	+13.09	+14.84	+16.93	+19.15	+14.62	+16.55
2	+13.04	+14.79	+16.86	+19.05	+13.85	+15.75
3	+12.84	+14.49	+16.38	+18.70	+11.15	+12.75
4	+12.00	+13.53			+ 5.29	+ 6.30
	A_2 = REFRACTIONATION OF A_1		B_2 = REFRACTIONATION OF B_1		C_2 = REFRACTIONATION OF C_1	
1	+13.60	+15.37	+16.97	+18.95	+15.96	+16.02
2	+13.67	+15.45	+17.73	+20.0	+16.00	+18.05
3	+13.75	+15.47	+17.63	+20.0	+16.25	+18.31
4	+13.60	+15.45	+17.65	+19.99	+15.92	+17.90
5	+13.56	+15.26	+17.80	+20.05	+15.77	+17.85
6	+13.15	+14.87	+17.65	+20.0	+15.65	+17.65
	A_3 = REFRACTIONATION OF A_2		B_3 = REFRACTIONATION OF B_2		C_3 = REFRACTIONATION OF C_2	
1	+13.75	+15.45	+17.88	+20.20	+16.00	+18.00
2	+13.67	+15.40	+17.70	+20.00	+16.01	+18.05
3	+13.80	+15.52	+17.70	+20.05	+16.01	+18.07
4	+13.75	+15.57	+17.85	+20.14	+16.15	+18.20
5	+13.80	+15.55	+17.80	+20.10	+15.95	+18.06
6	+13.78	+15.53	+17.85	+20.20	+15.57	+17.58
7	+13.78	+15.53	+17.82	+20.13		
8	+13.73	+15.53	+17.67	+20.00		
9	+12.98	+15.69				
	SLASH PINE					
	A_1 = FIRST 4 FRACTIONS FROM A		B_1 = FIRST 4 FRACTIONS FROM B		C_1 = FIRST 4 FRACTIONS FROM C	
1	−27.81	−31.31	−27.70	−31.19	−28.18	−31.78
2	−27.81	−31.31	−28.18	−31.86	−28.21	−31.81
3	−27.56	−31.14	−28.18	−31.95	−27.98	−31.48
4	−26.61	−29.81	−28.20	−31.75	−26.96	−30.16
	A_2 = REFRACTIONATION OF A_1		B_2 = REFRACTIONATION OF B_1		C_2 = REFRACTIONATION OF C_1	
1	−27.86	−31.51	−28.21	−32.01	−28.31	−31.96
2	−27.86	−31.51	−28.31	−32.01	−28.42	−32.15
3	−27.96	−31.66	−28.50	−32.21	−28.31	−31.96
4	−26.21	−29.35	−28.51	−32.11	−28.59	−32.36
			−28.71	−32.31	−28.71	−32.37
			−25.22	−27.96	−25.76	−28.61

[a] A. Sample taken from 51 gallons of distillate collected at beginning of run (first 5 gallons distillate taken in another vessel).
B. Sample taken from next 51 gallons of distillate collected.
C. Sample taken from remainder of distillate collected.
A, B, and C were each fractionally distilled in the laboratory. The first three or four fractions of each (designated under A, B, C, respectively) were refractionated, giving a series of fractions. The first six or four fractions of these (designated under A_2, B_2, C_2, respectively) were again refractionated (in case of long-leaf pine). giving the series under A_3, B_3, C_3.

[b] 578 mμ.

[c] 546 mμ.

Rotatory dispersion and density data corresponded well with those reported by Dupont and Desalbres (*6*). According to these authors, repeated fractional distillation of even pure α-pinene yields fractions of slightly higher rotations owing to the tendency of inactive pinene to concentrate in the top fractions.

TABLE II. COMPONENT DISTRIBUTION AND PROPERTIES OF TURPENTINE SAMPLES

SAMPLES	COMPOSITION OF SAMPLES			PROPERTIES OF SAMPLES			
	α-Pinene %	β-Pinene %	Tailings %	Observed rotation (J = 578 mμ)	(V = 546 mμ)	n_D^{25}	$d_{15.6}$
				LONG-LEAF PINE			
A[a]	59.1	38.5	2.46	+0.94°	+1.49°	1.4688	0.8669
B	57.5	39.5	2.95	+2.95°	+3.89°	1.4692	0.8670
C	50.65	45.7	3.63	−0.68°	−0.14°	1.4703	0.8695
1st 46% of distn.[b]	59	38.5	2.45	.....	.....	......	......
1st 85% of distn.[b]	58	39	2.7	.....	.....	......	......
Last 15% of distn.	50.6	45.7	3.6	.....	.....	......	......
Whole turpentine[b]	57	40	2.8	+1.52°[b] +1.76°[c]	+1.41[c]	......	......
				SLASH PINE			
A	58.8	37.4	3.83	−23.69	−26.15°	1.4695	0.8670
B	51.2	43.7	5.03	−23.47	−25.90°	1.4701	0.8674
C	42.8	50.4	6.79	−22.21	−24.31°	1.4716	0.8684
1st 46% of distn.[b]	59	37	3.8	.....	.....	......	......
1st 85% of distn.[b]	55	40.5	4.4	.....	.....	......	......
Last 15% of distn.	43	50	6.8	.....	.....	......	......
Whole turpentine[b]	53	42	4.75	−23.42°[b] −23.88°[c]	−26.46°[c]	......	......

[a] See Table I, footnote *a*.

[b] Determined by calculation from samples A, B, and C.

[c] On turpentines obtained by steam distillation (in the laboratory) of gum samples taken from the original charges, the turpentine yields being 21.9% for the long-leaf and 21.6% for the slash pine. The quantities were too small, however, to permit determination of composition by the method described.

Presumably, complete and thorough mixing of the gum would have yielded an α-pinene of uniform optical value for all three of the subsamples from any one complete charge. As may be observed from Table I, this was nearly accomplished in the case of the slash pine. Appreciable difference, however, was noted in the case of the long-leaf pine. Such differences in rotation can hardly be ascribed to the presence of nonpinene constituents, such as the low-boiling hydrocarbons obtained by Chavannes (*3*) on fractionating French turpentine, since the rotations of the respective α-pinenes here became virtually constant after the first refractionation. Doubtless owing to the thick viscous character of the gum, thorough mixing of so large a mass was not accomplished with the field facilities available, and, further, owing to the poor thermal conductivity of the gum, uniform heating throughout the mass was nearly impossible.

The agreement in rotation values of the pure α-pinene components was much closer between the last two samples of each set than between the first and second. This may be expected, since the mass became progressively more uniform as the agitation by the steam distillation process itself progressed. Since each of the turpentine samples was treated as an independent entity (the α-pinene rotation being determined separately for each), any imperfection in the mixing of the gum did not affect the calculations on the turpentines.

Table II gives the summarized data on the component distribution and properties of the turpentine distillates from the two commercial charges of long-leaf and slash gum. Thus, in the case of the long-leaf run, the first 85 per cent of the distillate yielded a turpentine with an α-pinene content about 7 per cent higher and with a tailings content 0.9 per cent less, than the last 18 gallons. There is no reason to believe that the latter portions of the respective runs would be less desirable as a solvent or a paint thinner than the whole turpentine.

By changing the receiving vessel at a similar point in distilling the slash pine (in which the tailings content of the whole turpentine is 4.75 per cent), a pronounced improvement in tailings freedom is effected, the first 85 per cent showing an average of 2.4 per cent less tailings than the last 15 per cent.

Considerable difference is evident in the rectifying tendency of the two runs, particularly when the first 51-gallon distillates are compared. In view of the many variable factors involved, greater uniformity in distribution data is hardly to be expected. The data obtained in these experiments, although only approximately indicative of the general rectifying tendency prevailing under normal conditions in the fire still, show that both tailings and β-pinene tend to concentrate perceptibly in the last 15 per cent of the run. Thus the proportion of β-pinene in the last 18 gallons or so of distillate was higher than that in the whole turpentine by 6 to 8 per cent. Conversely, fractions from 2 to 6 per cent higher in α-pinene content and about 0.4 to 1 per cent lower in tailings content were obtained by taking the first 51 gallons of distillate, than if the whole turpentine were taken.

The improvement effected with regard to tailings, while apparently not great, is more significant than the absolute figures would indicate (*4*). The turpentines here considered were of exceedingly good quality, particularly the long-leaf, and the tailings content was less than that ordinarily found in turpentine of commerce (*5*, *8*).

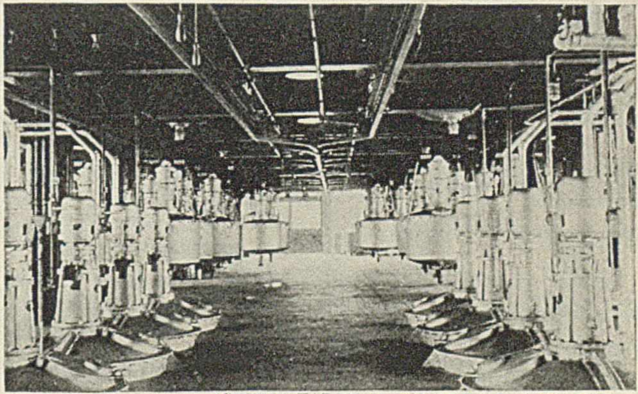
ACKNOWLEDGMENT

The samples of turpentine from the two species of pine were taken from runs made in a commercial still, and were obtained from D. F. Howell of Olustree, Fla., through the kind coöperation of C. F. Speh of the Pine Institute of America. Drawings were made by R. M. Baker of the Chemical Engineering Division of this bureau.

LITERATURE CITED

(1) Aschan, O., "Naphthenverbindungen Terpene und Campherarten inkl. Pinusharzsäuren sowie Körper der Kautschukgruppe," W. de Gruyter & Co., Berlin, 1930.
(2) Austerweil, G., French Patent 621,954 (Feb. 14, 1927).
(3) Chavannes, G., *Bull. soc. chim. Belg.*, **39**, 402–11 (1930).
(4) Dupont, G., *Chimie & industrie*, **8**, 549–58 (1922).
(5) Dupont, G., and Barraud, M., *Bull. inst. pin*, **1929**, 155–6.
(6) Dupont, G., and Desalbres, L., *Bull. soc. chim.*, **33**, 1252–62 (1923).
(7) Palkin, S., IND. ENG. CHEM., Anal. Ed., **3**, 377 (1931).
(8) Palkin, S., U. S. Dept. Agr., *Tech. Bull.* **276** (1931).
(9) Veitch, F. P., and Grotlisch, V. E., *Ibid.*, *Bull.* **898**, revised (1921).
(10) Vèzes and Dupont, "Résines et térébenthines. Industries dérivées," pp. 284–7, J. B. Baillière & Fils, Paris, 1924.

RECEIVED January 12, 1932.



Courtesy E. I. du Pont de Nemours & Co., Inc.

SHOWING LARGE AND SMALL MIXERS, DULUX ENAMEL BLDG., PHILADELPHIA, PA.

Composition of Corn Sirup Unmixed

A. P. Bryant and R. C. Jones
Clinton Corn Syrup Refining Co., Clinton, Iowa

Corn sirup, unmixed, is one of the most important raw ingredients used in the manufacture of confectionery, mixed sirups, and a large variety of other products. In spite of the fact that it is produced in large quantities, its exact composition is difficult to determine because of the presence of two reducing sugars, dextrose and maltose, as well as reducing dextrins and reversion products such as gallisin or isomaltose. In Browne's book (*4*) is given a diagram proposed by Rolfe[1] showing the supposed relation between specific rotation and composition of starch conversion products.

Allen (*2*) gives a discussion of commercial corn sirup and similar products with illustrative tables. These, however, do not seem to give a trustworthy value for the composition of corn sirup, unmixed.

Wesener and Teller (*6*) fermented corn sirup, unmixed, and calculated the sugars from gas evolved obtaining the following results based on total carbohydrates:

	%	%
Maltose	20.2	28.8
Dextrose	21.1	14.8
Dextrins	58.7	56.4
Total reducing sugars as:		
Dextrose	42.3	38.9
Dextrins	57.7	61.1

Bryant (*5*) gave results of examination of a number of samples of corn sirup, unmixed, the basis of the method being fermentation of reducing sugars.

Allen (*1*) states:

> The quantitative fermentation of sugars requires from six to seven days or longer if maltose is to be fermented in presence of dextrines. The use of yeast affords practically the only method for separating dextrose from maltose in the analysis of starch syrups. . . . The application of pure culture yeasts to the separation of different sugars promises valuable results. The sugar not attacked by the yeast in a mixture of fermentable and unfermentable carbohydrates can be estimated accurately; the estimation of the quantity of the fermented sugar from the carbon dioxide lost does not always give trustworthy results.

After considerable investigation of the possibility of obtaining pure cultures of yeast which would ferment dextrose and not maltose, or maltose and not dextrose, this analytical approach was given up, especially in view of the discouraging letters received from those who had tried out the method; it was decided to work farther along the line of fermentation of reducing sugars in corn sirup, unmixed, by means of ordinary bakers' yeast, thus carrying on the investigations started by one of the authors (*5*) some years ago. In the earlier experiments, brewers' yeast was used, but in the investigations here reported it was necessary to use fresh bakers' yeast.

Method of Procedure

The original material was carefully analyzed for total reducing sugars as dextrose, protein, and ash, and the results were calculated to dry basis.

The sirups were then made to approximately 10° Brix; 500 to 600 cc. were transferred to large flasks; the actual dry substance was determined by weighing on sand; and the weight of the reducing sugars as dextrose, protein, and ash in 100 cc. of the solution was computed.

The approximately 10 per cent solutions were polarized in a Bausch and Lomb saccharimeter, and the specific rotation calculated from the readings on the sugar scale and the dry matter found present.

Five grams of fresh bakers' yeast, thoroughly washed, were added to each flask, and volume and weight were noted. Fermentation was carried on at about 80° F. (26.7° C.) until there was no further loss of weight during 24 hours. This took from 6 to 10 days. A blank was run with each series of experiments taking 5 grams of washed yeast in 500 cc. of 4 per cent alcohol, the alcohol being added to prevent bacterial decomposition.

Table I. Results of Fermentation Experiments on Corn Sirup

	Low Conversion Sirup					Medium Conversion Sirup					High Conversion Sirup				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	Grams	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*
a. Carbohydrates in 100 cc.	10.26	10.75	8.78	10.27	10.24	10.11	8.78	10.33	10.43	10.52	10.16	10.59	10.39	10.36	10.44
b. Reducing value of same as dextrose	3.66	3.83	2.87	3.10	3.08	4.63	3.70	4.74	4.60	4.63	5.31	5.53	5.47	5.44	5.47
c. Unfermented carbohydrates in 100 cc.	6.67	7.09	5.31	6.91	6.43	5.39	4.30	5.10	5.32	5.31	5.40	5.66	4.87	4.11	4.32
d. Reducing value of same as dextrose	1.01	1.13	0.48	0.93	0.84	0.95	0.42	1.01	0.84	0.88	1.20	0.93	1.04	0.74	0.74
e. Total fermented $= a - c = F$	3.59	3.66	3.47	3.36	3.81	4.72	4.48	5.23	5.11	5.21	4.76	4.93	5.52	6.25	6.12
f. Apparent dextrose fermented $= b - d = K$	2.65	2.70	2.39	2.17	2.24	3.68	3.28	3.73	3.76	3.75	4.11	4.60	4.43	4.70	4.73
Maltose $= (F - K) \div 0.41$	2.29	2.34	2.64	2.90	3.83	2.54	2.93	3.66	3.30	3.56	1.59	0.81	2.66	3.78	3.39
Dextrose $= F -$ maltose	1.30	1.32	0.83	0.46	0	2.18	1.55	1.57	1.81	1.65	3.17	4.12	2.86	2.47	2.73
Dextrins $= c$	6.67	7.09	5.31	6.91	6.41	5.39	4.30	5.10	5.32	5.31	5.40	5.66	4.87	4.11	4.32
Percentages on carbohydrates:															
Maltose	22.3	21.8	30.1	28.2	37.4	25.1	33.4	35.4	31.6	33.9	15.6	7.6	25.6	36.5	32.5
Dextrose	12.7	12.3	9.6	4.5	0	21.6	17.6	15.2	17.4	15.7	31.2	38.9	27.5	23.8	26.1
Dextrins (unfermentable)	65.0	65.9	60.3	67.3	62.6	53.3	49.0	49.4	51.0	50.4	53.2	53.5	46.9	39.7	41.4
Ratio dextrose to maltose	1:1.8	1:1.8	1:3.1	1:6.2	....	1:1.2	1:1.9	1:2.4	1:1.8	1:2.2	1:0.5	1:0.2	1:0.9	1:1.5	1:1.2
Percentages as usually reported:															
Reducing sugars as dextrose	35.7	35.7	32.7	30.1	30.1	45.8	42.1	45.9	44.0	44.0	52.1	52.2	52.4	52.4	52.4
Dextrins by difference	64.3	64.3	67.3	69.9	69.9	54.2	57.9	54.1	56.0	56.0	47.8	47.8	47.6	47.6	47.6
Sp. rotation:															
Original	153°	153°	162°	159°	159°	135°	148°	135°	141°	141°	128°	128°	125°	125°	125°
Unfermentable	177°	182°	141°	174°	170°	166°	125°	157°	163°	159°	159°	138°	151°	157°	147°

---

[1] *The Polariscope*, 1905, 197.

The contents of the flasks were made up to original volume with distilled water, clarified by filtering through Filter-Cel; dry substance, reducing sugars as dextrose, protein, and ash, and angular rotation were determined. These results were calculated to values per 100 cc. The blank was analyzed in a similar way, and corrections for soluble solids therein were applied to the fermented residues. In no case was any reducing value or rotation observed in the blank.

In the earlier experiments no yeast food or accelerator was added. In one set of experiments a "buffer" solution containing sodium citrate, citric acid, and ammonium acid phosphate was added, but there were so many complications introduced that the results were unsatisfactory. In later experiments a little "Arcady," a preparation used by bakers, was added. Tables I and II summarize the results and give computed composition of the different samples. In these, samples 1 and 2 were duplicates on the same lot of sirup. Sample 3 represented another lot, and samples 4 and 5, duplicates on a third lot. Samples 6, 7, and 8 were separate lots, and samples 9 and 10 were duplicates. Samples 11 and 12 were duplicates on a highly converted corn sirup, and samples 13, 14, and 15 were triplicates on another similar sirup.

TABLE II. OTHER FERMENTATION TESTS

	Maltose (Av. 3 Tests)	Dextrose (Av. 5 Tests)	Sugar No. 70 (1 Test)	Barley Malt Sirup (1 Test)
	Grams	*Grams*	*Grams*	*Grams*
a. Carbohydrates in 100 cc.	9.60	10.61	10.52	9.21
b. Reducing value of same as dextrose	5.47	10.15	8.97	5.03
c. Unfermented carbohydrates in 100 cc.	0.41	0.42	1.50	1.36
d. Reducing value of same as dextrose	0.07	0.03	0.37	0.45
e. Total fermented $= a - c = F$	9.19	10.19	9.02	7.85
f. Apparent dextrose fermented $= f - d = K$	5.40	10.12	8.60	4.58
Maltose $= (F - K) \div 0.41$	9.22	0.17	1.02	0.0
Dextrose $= F -$ maltose	0.0	10.02	8.00	7.85[a]
Dextrins $= c$	0.38	0.42	1.50	1.36
Percentages on carbohydrates:				
Maltose	96.0	1.6	9.7	85.2
Dextrose	0.0	94.5	76.0	0.0
Dextrins (unfermentable)	4.0	3.9	14.3	14.8
Sp. rotation (original)	141°	54.7°	54.5°	92°

[a] Actual figures 8.00, indicating error in factor.

In determining the reducing value of the unfermentable residue, it was frequently necessary to resort to back titration as follows: Take 15 to 25 cc. of the unfermented solution and add to 25 cc. of boiling Fehling's solution, completing the reduction of the Fehling's solution by means of a 1 per cent dextrose solution. In this way it is possible to determine accurately the amount of reducing sugars as dextrose even when present in very small amounts.

In order to prove the applicability of this method in dilute solutions of maltose and dextrose, tests were made on solutions containing from 0.1 to 1 gram dextrose in 100 cc., and 0.25 to 2 grams of maltose in 100 cc.; it was found that the dilution had no appreciable effect upon the relative reducing value.

COMPUTATION OF AMOUNTS OF DEXTROSE AND MALTOSE

The ratio of reducing power of maltose to that of dextrose varies through quite wide limits, depending apparently upon exact method employed. The more commonly accepted ratio is 1 to 0.61, but this appears to be too large. Experimental work indicates that the ratio is more nearly 1 to 0.5875, or approximately 1 to 0.59 and this latter factor is used in the computations in the tables. The amount of dextrose equivalent to 25 cc. of standard Fehling's solution is 125 mg. Taking the amount of anhydrous maltose corresponding to 125 mg. of dextrose as shown in Munson and Walker's tables (*3*) gives the factor 0.579.

The following equations determine relative amounts of dextrose and maltose from the analytical data given in Tables I and II.

Let D = dextrose
M = maltose
K = reducing value as dextrose
F = amount fermented

$$D + M = F$$
$$D + 0.59\,M = K$$
$$\overline{}$$
$$0.41\,M = F - K$$
$$F - M = D$$
$$\text{Total solids} - F = \text{dextrins}$$

In order to compare the results reported with those made in a similar way by one of the authors (*5*), Table III summarizes these earlier results, but with the factor 0.59 for relative reducing power of maltose as compared with dextrose, instead of the factor 0.62 as previously used.

TABLE III. SUMMARY OF EARLIER RESULTS ON ANALYSIS OF CORN SIRUP BY FERMENTATION METHOD (*5*)

	Sample				Av. of Samples		
	N	O	K	D	E, F, G, H, & L	A, B, & C	I & M
	%	%	%	%	%	%	%
Maltose	28.6	25.2	26.0	28.3	29.2	31.2	29.8
Dextrose	2.2	10.6	14.2	16.5	17.4	20.8	23.1
Dextrin	69.2	64.2	59.8	55.2	53.4	48.0	47.1
Ratio dextrose to maltose	1:13	1:2.4	1:1.8	1:1.7	1:1.7	1:1.5	1:1.3
Percentages as usually reported:							
Reducing sugars as dextrose	29.3	36.5	40.3	42.4	44.0	48.3	50.2
Dextrins by difference	70.7	63.5	59.7	57.6	56.0	51.7	49.8
Sp. rotation (original)	155°	146°	143°	139°	138°	135°	132°

The maltose was bought as C. P. and was not recrystallized. The dextrose was a highly refined corn sugar and had a reducing value equivalent to 99.7 per cent pure dextrose. Both the maltose and dextrose gave a small amount of unfermented residue with a trace of reducing value. All residues were corrected for carbohydrates in the yeast blank which usually amounted to about 0.100 gram per 100 cc.

The final results on the sirups show considerable variation and indicate that the method requires further refinement by closer control and more uniform yeast, but prove conclusively the presence of a large proportion of maltose and noticeable amounts of unfermented matter which reduce Fehling's solution.

Some of the variations between different lots of similar sirup may be due to manufacturing conditions, but it seems probable that the activity of the yeast and other experimental factors had considerable bearing on these variations.

CONCLUSIONS

While the fermentation method of analyzing corn sirup is not entirely satisfactory and has many possibilities of error, it seems to be, everything considered, the method giving the closest approach to a knowledge of the actual proportions of maltose, dextrose, and dextrins.

The maltose content of the total carbohydrates remains around 30 per cent up to the higher conversions, and then appears to drop.

There are present noticeable amounts of unfermentable reducing compounds which can hardly be considered as reversion products but rather as reducing dextrins.

The total reducing sugars as dextrose give a fairly close measure of the sum of maltose and dextrose.

The ratio of dextrose to maltose is not far from 1:2 for ordinary conversions but nearer 1:1 in higher conversions.

For ordinary work and ordinary corn sirup one-third of the total reducing sugars as dextrose may be taken as actual dextrose, and two-thirds as maltose, calling the undetermined carbohydrates "dextrins."

LITERATURE CITED

(1) Allen, "Commercial Organic Analysis," 5th ed., Vol. I, p. 431, Blakiston, 1923.
(2) *Ibid.*, p. 473, *et seq.*
(3) Assoc. Official Agr. Chem., Methods of Analysis, 2nd ed., p. 440 (1925).
(4) Browne, Handbook of Sugar Analysis, 1st ed., p. 507, Wiley, 1912.
(5) Bryant, A. P., *8th Intern. Congr. Applied Chem.*, **13**, 47 *et seq.* (1912).
(6) Wesener and Teller, J. Ind. Eng. Chem., **8**, 1009 (1906).

RECEIVED July 13, 1932. Presented before the Corn Products Symposium at the 11th Midwest Regional Meeting of the American Chemical Society, St. Louis, Mo., May 6 to 7, 1932.

Change of Crude Lipides of Wheat on Storage

B. SULLIVAN AND CLEO NEAR, Russell-Miller Milling Co., Minneapolis, Minn.

Wheat and its products were extracted with various fat solvents and the phosphorus and nitrogen contents of the extracts measured.

Under different storage conditions the amounts of extracts and their phosphorus and nitrogen showed marked variation. The changes observed are explained as being due to enzymic hydrolysis and are correlated with increasing moisture and acidity of the samples.

The nitrogen-phosphorus ratios of all the extracts were greater than 1 to 1, indicating the presence of nitrogen-containing lipides other than lecithin.

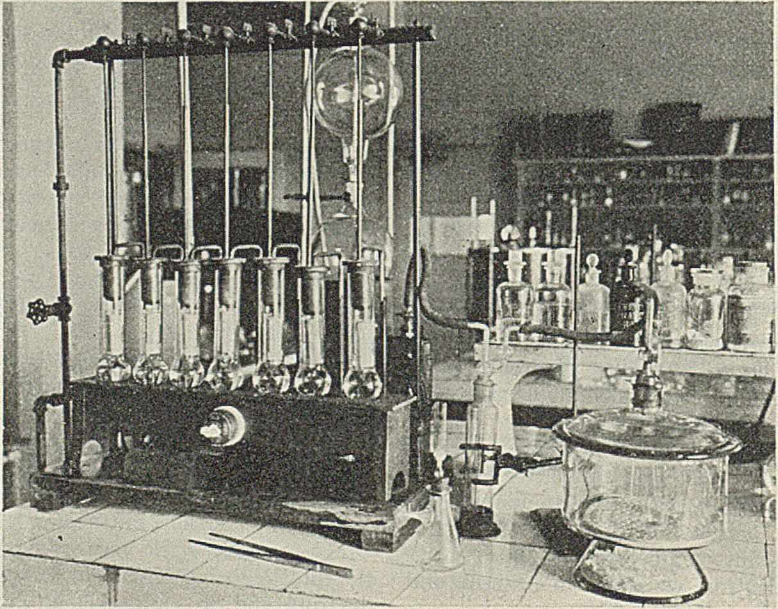
IN PREVIOUS publications from this laboratory (*2–5*) a method for the estimation of the lipides of wheat and its products has been given and the importance of these compounds in relation to gluten quality has been stressed. The term "lipides" as it is used in this paper includes the fats, fatty acids, their neutral esters, and other compounds in wheat, such as the phospholipides and glycolipides, which yield fatty acids on hydrolysis. Small amounts of sterols, waxes, and plant pigments, in addition to traces of other extraneous substances having no chemical relationship to the fats, are always present when a plant product is extracted with any of the so-called fat solvents. Different solvents extract varying amounts of the fats and fat-like compounds, and consequently the extracts are generally named according to the solvent used instead of the substance extracted, with the exception of the alcohol-ether extract. The alcohol-ether extract of a plant tissue which has been evaporated to dryness and then taken up in chloroform has been referred to by many writers, including the authors, as "lipoids." Since this term has been used by different investigators in such different and conflicting manners, it was thought advisable to refer to the alcohol-ether extract as such.

In an effort to isolate pure lecithin as well as to ascertain the presence or absence of sphingomyelin, cerebrosides, and other lipides in the different milling separations of wheat, it was thought advisable to measure first the amount of lipide material extracted by various solvents, and by determining the nitrogen and phosphorus content of the crude lipides, gain a rough indication as to which of the solvents was the most effective in removing the compounds in which we were interested. At the beginning of this work it was found difficult to secure closely agreeing results on some of the extracts from wheat germ and bran unless the extractions were done the same day. The reason for this was found later. Samples were sealed in moisture-proof containers to prevent evaporation of moisture, and it was on material kept in this way that closely agreeing results were difficult to secure when extractions were done at different times. Samples stored in the air in cotton bags, on the other hand, showed little or no change.

EXPERIMENTAL PROCEDURE

All the samples used in this investigation were milled in a 3000-barrel mill from northwest hard spring wheat. The analyses of the wheat and its products are given in Table I. Total phosphorus was determined in the ash by means of the standard gravimetric method and calculated to the product.

Extractions were conducted in a Soxhlet extraction outfit using an electric hot plate and Bailey Walker condensers. Chemically pure solvents were used in every case, the ether in addition being dried and kept over sodium. In the case of wheat and flour, the samples were mixed with pumice to prevent packing in the alcohol-ether extraction. Previous to extraction all the samples were dried for 20 minutes at 70° C. and 100 mm. pressure. All extractions except the alcohol-ether were conducted for 16 hours. It was necessary to filter



FAT EXTRACTOR USED IN EXPERIMENTS

all the extracts except the ether through a Bertrand asbestos filter before evaporating to dryness and constant weight at 70° C. and 100 mm. pressure.

Table I. Analyses of Products

(Results calculated to dry basis)

	Germ	Bran	Wheat	Patent Flour
Protein, %	33.40 (N × 6.25)	21.69 (N × 6.25)	16.77 (N × 5.7)	14.20 (N × 5.7)
Ash, %	4.82	6.53	2.05	0.47
Phosphorus, %	1.133	1.478	0.451	0.111

The extract termed "alcohol-ether" was obtained by extracting the samples with 95 per cent alcohol for 2 hours and then with ether for 2 hours, except in the case of ground bran, where it was found necessary to reflux overnight with alcohol, as the extraction at the end of 2 hours was not complete. The combined alcohol and ether extracts were evaporated to dryness on a boiling water bath and the residue taken up in chloroform, filtered, and evaporated to constant weight at 70° C. and 100 mm. pressure. Hot alcohol extracts practically all the lipide material, the ether being used merely to remove the last traces. In all cases the alcohol-ether extract had a higher percentage of phosphorus than any of the other extracts. In order to prove that the alcohol-ether extraction procedure removed the maximum amount of phosphorus-containing lipides, extractions were done with 95 per cent alcohol for 16 hours, the extracts cooled to room temperature, filtered, and evaporated to dryness at 70° C. and 100 mm. pressure. The amount of the extract was not significant because of the contamination by gliadin, starch, and other impurities, but the total amount of phosphorus extracted was a very close check with the amount of phosphorus extracted by the alcohol-ether procedure on each product.

Phosphorus and nitrogen are reported as determined in the total lipides extracted by various solvents.

Phosphorus of the lipides was determined by the micromethod of Pregl (*1*) as follows:

From 0.1 to 0.5 gram of fat (depending on the phosphorus content) is mixed thoroughly with a 1 to 1 mixture of c. p. potassium nitrate and c. p. sodium carbonate. The mixture is ignited slowly on an open flame in a covered platinum dish. This heating must be done very cautiously since the mixture has a tendency to spatter. The mixture is then ignited in a muffle at 575° C. until white. The ignited residue is taken up in a solution of one part of nitric acid to 2 parts of water, filtered, and washed with hot water, with the volume carefully kept as small as possible. Then 2 cc. of the sulfuric–nitric acid mixture are added, the solution heated to 97° C., and shaken vigorously. Next, 15 cc. of sulfate-molybdate solution are made up to the same volume as the volume of the sample, and are then poured into the center of the sample without shaking. The resulting temperature should be 65° to 70° C. At the end of 3 minutes the solution is shaken for 30 seconds and then allowed to stand for one hour at room temperature. A Jena glass crucible No. 10G4, which has been previously washed with ammonia, water, nitric acid, water, alcohol, and ether, and dried for 30 minutes in a vacuum desiccator, is used for the filtration. The precipitate is washed alternately with 2 per cent ammonium nitrate and alcohol, then finally with alcohol and ether, dried for 30 minutes in a vacuum desiccator, and weighed.

The factor used was 0.01453 for converting the yellow precipitate to phosphorus. Experiments were conducted using different temperatures and volumes in the precipitation of the yellow precipitate. It was found that when the above procedure was followed, the results checked closely with the standard gravimetric procedure in which the phosphorus is weighed as magnesium pyrophosphate. The solutions for the Pregl method were made up exactly as given by Pregl (*1*).

The following procedure was used in determining the nitrogen in the lipides:

From 0.2 to 0.5 gram of fat was taken up in ether and transferred to a Kjeldahl flask, and the ether evaporated. Nitrogen was determined according to the regular Kjeldahl method using potassium sulfate with mercury as a catalyst. Sulfuric acid and sodium hydroxide, both 0.02 *N*, were used for the titration with sodium alizarin sulfonate as the indicator.

The official A. O. A. C. method was used for the acidity determination, and the results calculated as lactic acid except on the germ. The end points given by the germ with both the official and the Greek methods were unsatisfactory, but the Greek acidity method was preferable, and results by this method, in line with common practice, were reported as sulfuric acid.

Moisture was determined by the 130° C. air oven method.

Wheat and samples of germ, bran, and patent flour milled from it were taken from the mill on different dates in order to have fresh samples for analysis. The analyses on the original samples in each case were done as rapidly as possible to prevent any change. A part of each original sample was placed in a glass container and the stopper sealed with paraffin. Another part of each sample was stored in a cotton bag in the laboratory at room temperature. Months later both the samples in the sealed containers and the cloth

Table II. Change of Lipides on Storage

(Results calculated to dry basis)

	Original Sample				Sample Sealed in Container with High Moisture for 3 Months			Sample Stored in Bag for 3 Months		
	Extract	P	N	Ratio N:P	Extract	P	N	Extract	P	N
	%	%	%		%	%	%	%	%	%
	13.7% moisture and 0.111% acidity as H_2SO_4				13.6% moisture and 0.510% acidity as H_2SO_4			8.2% moisture and 0.139% acidity as H_2SO_4		
Germ:										
Alcohol-ether	15.24	0.518	0.39	1.7:1	13.41	0.197	0.15	14.07	0.500	0.32
Ether	12.05	0.114	0.08	1.6:1	12.74	0.018	0.03	12.40	0.129	0.07
Acetone	13.06	0.164	0.23	3.1:1	14.22	0.055	0.16	13.19	0.133	0.27
Ethyl acetate	13.16	0.268	0.22	1.8:1	14.11	0.052	0.11	13.54	0.233	0.35
	13.9% moisture and 0.568% acidity as lactic acid				13.8% moisture and 1.22% acidity as lactic acid			8.0% moisture and 0.93% acidity as lactic acid		
Bran:										
Alcohol-ether	7.36	0.464	0.31	1.5:1	7.05	0.093	0.19	7.39	0.458	0.41
Ether	5.60	0.091	0.13	3.2:1	6.50	Trace	Trace	5.58	0.105	0.18
Acetone	7.05	0.150	0.19	2.8:1	7.59	0.029	0.12	7.13	0.163	0.22
Ethyl acetate	7.26	0.248	0.18	1.6:1	7.53	0.019	0.10	6.92	0.229	0.28
	14.8% moisture and 0.351% acidity as lactic acid				13.5% moisture and 0.495% acidity as lactic acid			9.5% moisture and 0.345% acidity as lactic acid		
Wheat:										
Alcohol-ether	3.16	0.481	0.38	1.8:1	2.99	0.238	0.32	3.16	0.511	0.45
Ether	2.50	0.145	0.33	5.0:1	2.62	0.063	0.21	2.44	0.128	0.31
Acetone	3.19	0.188	0.27	3.2:1	3.30	0.115	0.25	3.04	0.204	0.30
Ethyl acetate	3.40	0.301	0.32	2.4:1	3.29	0.102	0.24	3.04	0.291	0.35
	13.6% moisture and 0.104% acidity as lactic acid				13.6% moisture and 0.116% acidity as lactic acid			6.7% moisture and 0.118% acidity as lactic acid		
Patent flour:										
Alcohol-ether	1.29	0.575	0.56	2.4:1	1.40	0.502	0.54	1.37	0.572	0.71
Ether	1.13	0.234	0.79	7.4:1	1.12	0.251	0.73	1.03	0.241	0.73
Acetone	1.25	0.433	0.40	2.0:1	1.27	0.322	0.35	1.23	0.382	0.45
Ethyl acetate	1.20	0.302	0.32	2.3:1	1.21	0.329	0.27	1.10	0.277	0.34

bags were analyzed and compared with the results on the original fresh samples. Those sealed in the glass containers maintained their original moistures very closely and the samples in the bags lost several per cent of moisture by gradual evaporation.

DISCUSSION

The differences in the analyses of the samples stored under different conditions are very marked in the case of the germ, bran, and wheat, but only slight in the patent flour, as shown in Table II. These changes on storage explain the differences in the phosphorus of the alcohol-ether extract of wheat products as previously reported (*2*). The alcohol-ether extract on the germ, bran, and wheat dropped considerably on the samples stored in the sealed containers at or near their original moisture content—as much as 2 per cent in the case of the germ. The phosphorus and nitrogen content of all these alcohol-ether extracts decreased, the phosphorus dropping to less than half the original amount. However, the ether, acetone, and ethyl acetate extracts increased in amount, although the phosphorus and nitrogen in all cases decreased as in the alcohol-ether extracts. It will be noted that on the germ, bran, and wheat the acetone and ethyl acetate extracts increased to such an extent that they became higher in amount than the alcohol-ether extracts, although the material extracted by acetone and ethyl acetate always contained less phosphorus. The analyses of the bran and wheat samples stored in bags gave almost perfect checks throughout with the original samples when all results were calculated to dry basis. The germ, however, showed a slight change in the same direction as the sample which had been kept near its original moisture by storage in the sealed container. The changes taking place in the germ were rapid, it being difficult to obtain closely agreeing results even a few days after the original test because of the activity of the enzymes in germ at the relatively high moisture content before natural evaporation could take place. The sample of patent flour showed little change in 3 months' time, although the tendency of the changes was in the same direction as those of the other products. For example, the phosphorus content of the alcohol-ether extract of the flour stored at its original moisture was 0.502 per cent, compared with the phosphorus on the original of 0.572 per cent.

TABLE III. ANALYSES OF WHEAT STORED UNDER VARIOUS CONDITIONS

(Results calculated to dry basis)

SOLVENTS	SAMPLE STORED IN BAG AS GIVEN IN TABLE II AT 9.5% MOISTURE		SAMPLE DIVIDED AND STORED AT DIFFERENT MOISTURES FOR 4 MONTHS IN SEALED CONTAINERS				WHOLE KERNELS IN SEALED CONTAINER FOR 7 MONTHS AT 14.1% MOISTURE		GROUND SAMPLE IN SEALED CONTAINER FOR 4 MONTHS (RESPIRATION) AT 14.8% MOISTURE	
			At 9.5% moisture		At 12.2% moisture					
	Extract	P	Extract	P	Extract	P	Extract	P	Extract	P
	%	%	%	%	%	%	%	%	%	%
Alcohol-ether	3.16	0.511	2.94	0.507	2.96	0.357	2.86	0.225	1.44	0.195
Ether	2.44	0.128	2.40	0.143	2.61	0.097	2.42	0.053	0.98	0.034
Acetone	3.04	0.204	2.92	0.167	3.02	0.132	3.16	0.143	2.41	0.086
Ethyl acetate	3.04	0.291	3.04	0.264	3.04	0.177	3.36	0.069	2.16	0.050

Table III gives results on the wheat stored under different conditions. Analysis is given for the wheat stored for several months as whole kernels in a sealed container with the original moisture, whereas the sealed sample in Table II was a ground sample, and shows the same change with a decided drop in phosphorus content of the extracts throughout. Quite by accident one sample of ground wheat sealed with the original moisture started respiration when it was opened, and its moisture content increased rapidly. The fat extracted by all the solvents showed a marked decrease, and the phosphorus content of the fat likewise decreased. The acetone and ethyl acetate extracts were considerably higher than the ether and the alcohol-ether extracts because the last two were done a week later, during which time the moisture continued to increase owing to respiration changes. The sample which had been in a bag for 3 months at 9.5 per cent moisture was divided, part stored at that moisture in a sealed container, and the other part placed over water to increase its moisture content several per cent and it, too, stored in a sealed container. At the end of 4 months the sample stored in a sealed container with 9.5 per cent moisture showed only a slight decrease in the phosphorus contents of all the extracts, but the one with 12.2 per cent moisture showed a very decided drop in phosphorus. This indicates that the higher moisture content rather than the anaërobic condition is responsible for the observed changes.

In order to obtain more evidence that the anaërobic condition was not responsible for the changes, a fresh sample of germ was taken. Table IV gives the analysis of this original germ, the same germ after 6 months' storage in a sealed container at the original moisture, and the same germ dried in a vacuum desiccator over Desicchlora down to 4 per cent moisture before storing in a sealed container for 6 months. The sample stored with the higher moisture showed a very marked decrease in the alcohol-ether extract, an increase in the ether and acetone extracts, and a decided drop in both phosphorus and nitrogen content, just as the germ sample in Table II. But the sample sealed with low moisture showed a relatively slight change in the phosphorus and nitrogen contents of the extracts, as compared with the sample stored at a higher moisture. These results indicate again that the moisture content is the predominant factor in causing a change in the amount and composition of the lipides extracted by different solvents.

TABLE IV. ANALYSES OF GERM STORED UNDER VARIOUS CONDITIONS

(Results calculated to dry basis)

	ORIGINAL SAMPLE			SAMPLE SEALED IN CONTAINER 6 MONTHS			SAMPLE SEALED IN CONTAINER 6 MONTHS		
Per cent moisture:	13.55			12.30			4.03		
Per cent acidity:	0.084 as H_2SO_4			1.27 as H_2SO_4			0.161 as H_2SO_4		
SOLVENTS	Extract	P	N	Extract	P	N	Extract	P	N
	%	%	%	%	%	%	%	%	%
Alcohol-ether	15.62	0.503	0.41	12.81	0.030	Trace	13.68	0.560	0.35
Ether	11.81	0.142	0.12	13.00	Trace	0.04	11.54	0.085	0.04
Acetone	12.58	0.128	0.34	14.60	0.040	0.05	12.23	0.094	0.23

The above brief discussion of results and the tables containing the complete data indicate that the changes observed are due to various fat-splitting enzymes, for example, lecithinase. Such enzymes are able to show greater activity at the higher moisture levels. The results show that the changes observed are due largely to hydrolysis rather than oxidation. When lecithin is split, fatty acids, such as stearic, palmitic, and oleic, are formed, together with choline and glycerolphosphoric acid. Pure lecithin is soluble in ether, but in wheat it is held with proteins and carbohydrates as a complex which is not completely soluble in ether until it has been split by treatment with alcohol. Hence in the original samples the amount of the ether extract is considerably lower than the alcohol-ether extract, and its phosphorus content is also much less. But the fatty acids which are split off upon enzymic hydrolysis of the lecithin are soluble in ether, increasing the amount of the ether extract. However, the glycerolphosphoric acid, or its cleavage products, and choline are insoluble in ether, and the amount of the phosphorus and nitrogen-containing material extracted by the ether is therefore less after hydrolysis has taken place.

Lecithin is reported in the literature as being insoluble in acetone. It is well recognized, however, that a considerable amount of the lecithin of natural products dissolves in acetone in the presence of other fats and fatty acids. The acetone and ethyl acetate, as well as the ether, extract more material after enzymic hydrolysis has taken place, owing to their greater ability to dissolve the fatty acids formed on hydrolysis than to dissolve the original lecithin. On the other hand, the alcohol-ether extraction removes all the lecithin of the original samples, but upon enzymic hydrolysis, although the fatty acids are still soluble, the choline and the glycerolphosphoric acid are less soluble in the ether and chloroform, both of which solvents give the same results when used in the last step in the alcohol-ether extraction. This decreases both the amount of the extract and its phosphorus and nitrogen content. An increase in acidity is correlated very definitely with increasing moisture content and with corresponding decreases in the phosphorus and nitrogen contents of the lipides. This increase in acidity is caused both by the fatty acids and the phosphoric acid liberated by the hydrolysis of the lipides.

Since in the case of the lipide material extracted by all the solvents the nitrogen-phosphorus ratio is more than 1 to 1, which is the ratio of these elements in lecithin, there must be some nitrogen-containing compound other than lecithin present in the extracts, such as sphingomyelin and galactolipides. The nitrogen-phosphorus ratios in the ether extracts of the original samples increase progressively from the germ to the patent flour, whereas there is no such marked difference in the nitrogen-phosphorus ratios on the other extracts. In the samples in which hydrolysis had taken place, the figures for phosphorus and nitrogen were in some cases so low that the ratios are not significant.

As might be expected, the changes observed were most marked in those parts of the wheat highest in fat content and in enzymic activity (germ and bran). Wheat, which contains roughly 25 per cent of germ and bran, likewise exhibits the same changes but not to the same degree. Flours, both patent and straight, showed only very slight changes in the amount of the lipides extracted by various solvents and in the phosphorus and nitrogen contents of the lipides regardless of storage conditions.

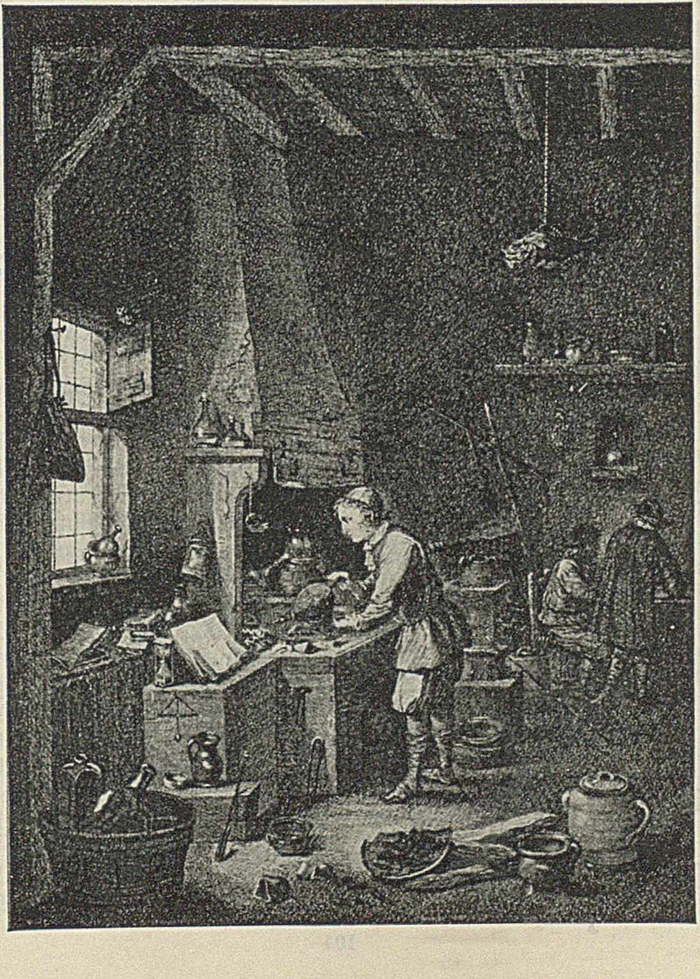
This investigation is being continued in an effort to isolate certain of the individual lipides of wheat and its products.

LITERATURE CITED

(1) Pregl, "Die Quantitative Organische Mikroanalyse," 2nd ed., pp. 151–8, Springer, 1923.
(2) Sullivan and Near, *Cereal Chem.*, 5, 163–8 (1928).
(3) Sullivan and Near, IND. ENG. CHEM., 19, 159–61 (1927).
(4) Sullivan and Near, *Ibid.*, 19, 498–501 (1927).
(5) Sullivan and Near, *J. Am. Chem. Soc.*, 49, 467–72 (1927).

RECEIVED July 12, 1932.

Le Jeune Chimiste
by
DAVID TENIERS,
the Younger



Our sixth Teniers reproduction is from an engraving by Jorma (anagram signature of Thomas Major, 1714–1799), a famous English engraver whose work was confined to the reproduction of paintings in London and Paris. Our thanks are extended to Dr. Charles A. Browne for permission to photograph his original engraving.

(Photographic copies of this reproduction, No. 24, can be obtained from D. D. Berolzheimer, 50 E. 41st St., New York, N. Y. See page 1173, October, 1932, issue for particulars.)

Post-War Progress in Various Industries

A Statistical Summary

Otto Wilson, 3025 Fifteenth St., Washington, D. C.

With the publication of the preliminary figures now being issued by the Bureau of the Census[1] covering the results of the 1931 census of manufactures we are receiving for the first time a fairly accurate statistical picture of the effect of the 1929 collapse on national industries. For chemical and related industries, that collapse climaxed a period of immense expansion, during which they trebled and quadrupled their pre-war output, besides admitting to their ranks a number of new industries based on newly discovered processes. The graphic record of these fourteen post-war years is written in the figures of the government census taken every two years. In 1932 the record up to the 1929 peak for the manufacture of commercial chemicals was presented.[2] The present article takes up the story for a number of industries related to chemistry, and adds to the record the 1931 census figures just being issued by the Government.

The history of these related industries corresponds in general to that of the purely chemical industries, and indeed of American industry as a whole. In 1919 the effect of war-inflated prices and abnormal war demand was still felt, and total value of production soared to great heights. It was swiftly cut down by the post-war liquidation, but recovered quickly and entered on the upward climb which carried it to the peak of 1929—a peak which as a rule stood even higher than that of ten years before and was several times as great as pre-war production. The abrupt drop of 1929, as revealed by the 1931 figures, reduced output 20 to 60 per cent or more in value, the average running about 35 to 40 per cent. Such staples as rayon and soaps were much less affected, but wood distillation products and ethyl alcohol felt the slump severely.

PAINTS AND VARNISHES

Manufacturers of paints and varnishes have no reason to complain that they did not share fully in the great industrial expansion of the last decade. When production reached its all-time high in 1929, the output of the paint and varnish industry (covering "Pigments or colors other than bone black, carbon black, and lampblack, paints in paste form, paints mixed ready for use, varnishes, lacquers, japans, enamels, fillers, stains, etc. ") was more than a half-billion dollars—$568,976,000. This was four times the total reached in 1914 and twice that of 1921; in the last thirty years it represented an eightfold growth.

The preliminary returns for 1931 show a drop of 39 per cent in value of output from 1929, the total standing at $348,855,000. This total, however, is still higher than for any census year prior to 1923, and is some two and one-half times the output of just before the war. Table I shows the value of production in the three great classes of commodities in this group as given in pre-war, post-war, and recent censuses.

A study of these figures reveals some interesting developments. At its peak in 1929 the production of paints, varnishes, and related products stood at a value almost four and one-half times as great as that of pre-war production in 1914. The slump in the two years following this peak, severe as it was, brought production down only some 38 per cent, leaving it still well above the inflated values of 1919 and more than two and one-half times as great as before the war. As compared with the fairly prosperous year 1923, it was about 13 per cent less but was 30 per cent above the output of 1921.

TABLE I. PRODUCTION OF PIGMENTS, PAINTS, AND VARNISHES IN U. S.[a]

(In thousands of dollars)

PRODUCTS	1914	1919	1921	1929	1931[b]
Pigments (colors)	$17,450	$72,457	$47,637	$116,753	$68,332
Paints:					
In paste form	29,038	49,183	46,603	46,666	26,030
Water paints and calcimines, dry and in paste form	2,055	4,549	4,395	7,093	5,258
Mixed, ready for use	41,691	120,145	91,180	178,242	118,345
Total, paints	72,785	173,877	142,178	232,001	150,840
Varnishes, japans, and lacquers (including enamels):					
Oleoresinous varnishes	[c]	40,045	29,034	47,740	29,455
Spirit varnishes (not turpentine)	[c]	8,106	7,255	13,535	7,835
Other varnishes	[c]	10,274	6,168	10,613	5,648
Pyroxylin products	[c]	923	3,094	82,336	46,578
Other products of varnish group	.....	27,978	25,726	50,657	34,403
Total varnishes, etc.	36,400	87,326	71,277	204,881	123,919
Other products (stains, fillers, etc.)	5,046	12,508	10,661	21,245	13,579
Grand total	131,681	346,168	271,753	574,880	356,670

[a] These figures cover not only the production of establishments engaged primarily in the manufacture of paints, varnishes, and related products, but also commodities of that kind produced as by-products in other industries. Except for 1914 and 1919 they do not include those products of paint and varnish establishments (such as containers or labels) which cannot be classified as paints and varnishes or related products, and the total value of which averages about 6 or 7 per cent of the value of all products of the industry. The totals in the table, therefore, differ slightly from those given above in the text, which cover the value of all products of paint and varnish establishments. The same general principle applies to other tables in this article showing production.

[b] Preliminary figures. [c] Not separately stated.

Most spectacular among the specific commodities in its advance were, as would be expected, the pyroxylin lacquers. Before the war they were of so little account that no separate returns were made for them. In the first year after the war they were still valued at less than a million dollars. Then they mounted steeply until in 1929 their total of $82,000,000 represented one-seventh of the value of all paint and varnish products made in this country. The greatest advance came in 1925–27, when output more than doubled, increasing from a value of $27,253,000 to $64,522,000. Of the total in 1929, clear lacquers constituted 9,939,000 gallons valued at $19,179,000; lacquer enamels, 15,151,000 gallons valued at $38,555,000; and thinners, 17,871,000 gallons valued at $19,151,000. The preliminary 1931 returns show an increased proportion of clear lacquers, which made up about 30 per cent of the whole, or 7,889,000 gallons valued at $12,673,000. The proportion of thinners (12,363,000 gallons valued at $10,978,000) was about the same as in 1929, whereas that of lacquer enamels (8,615,000 gallons valued at $20,618,000) was somewhat less. As these figures show, the valuation of

---

[1] All 1931 figures given are preliminary, but the Bureau of the Census, in compiling them, included returns from the larger manufacturers in a given industry and careful estimates for the few small ones whose reports were still to come in; the totals may be taken as approximately correct. As a convenience to manufacturers the Bureau of the Census, in gathering production figures for 1929, required reports of "shipments or deliveries" (sales) of the manufacturer's products instead of total production as in former years, and as in 1931. In the words of the Bureau, however, "It is believed that the change had very little effect on the comparableness of the statistics for 1929 with those for preceding census years" because excesses of production or of sales in different plants largely counterbalanced each other. In the present article the difference has been ignored.

[2] Wilson, O., Ind. Eng. Chem., 24, 388–97 (1932).

enamels dropped but slightly in 1931, standing at about $2.40 per gallon as against $2.54 in 1929, but that of clear lacquers fell from $1.93 to $1.60.

New Jersey is the leading state in the manufacture of pyroxylin products, accounting for about one-third of the clear lacquers in 1929, one-fourth of the enamels, and one-fourth of the pyroxylin thinners. Michigan surpassed New Jersey in amount of both enamels and thinners produced but was second in point of value in enamel production, and turned out only about one-sixth as much clear lacquer. Other leading states were Ohio, Pennsylvania, and Illinois.

In the paint industry the distinctive feature of the post-war development, aside from a threefold increase as compared with 1914, has been the striking advance of paints mixed ready for use, as against an almost stationary production of paste and dry paints. In 1914 the value of such ready-to-use paints totaled $41,691,000, which was about 57 per cent of all paints made. In 1929 and 1931 the proportion was almost 80 per cent. Oil paints naturally constitute the greater part ($96,732,000 in value in 1929 and $62,164,000 in 1931, or more than half in both years), but wall paints and mill whites, with about $32,000,000 in 1929, have been growing rapidly in favor and their 1931 total of $24,000,000 represented a drop of only about 25 per cent from that of two years before—much less than most other articles in this group.

As corollary to this trend toward ready mixed paints, production of pigments, or colors, for sale as such in 1931 fell below that of twelve years before, although it was still four times as great as before the war. In 1929 dry white lead made for sale was valued at $12,306,000 and in 1931 it dropped to $6,899,000. Production of litharge for sale fell from $12,965,000 to $5,565,000, the latter figure being only 30 per cent of that of six years before. Zinc oxide, the leading article of this group, was valued at $26,933,000 in 1929 as compared with $24,082,000 in 1919, and in 1931 it likewise dropped sharply to $14,051,000. Other items showed a like tendency toward small gains or actual decrease in 1929, as compared with preceding years, and abrupt declines in 1931. Chrome colors were a conspicuous exception to the latter rule. Chrome yellow output in 1931 was valued at $2,019,000 as against $2,393,000 in 1929, chrome orange at $1,267,000 as against $1,450,000, and chrome green at $2,550,000 in 1931 as against $2,603,000 in 1929.

Bone Black, Carbon Black, and Lampblack

The above figures do not include bone black, carbon black, and lampblack, for which separate returns are published by the Bureau of the Census. They are differentiated in the official reports as follows: "Bone black, also known as 'char' or animal charcoal, is produced by the carbonization of bone in retorts; carbon black by the imperfect combustion of natural gas; and lampblack by the imperfect combustion of coal or wood tar, petroleum, rosin, etc."

The total value of the three products, taken together, reached $20,170,000 in 1929, a great jump from the mark of the three preceding census years (1923–27) in which production had remained steady at about $14,500,000. The pre-war output was only about $1,400,000, which increased in 1919 to $6,186,000. The increase, however, was due almost wholly to gains in production of carbon black, which now makes up 75 to 85 per cent of the total. Before the war the whole output of carbon black was valued at less than a million dollars annually. In 1919 this had increased to $3,816,000. Ten years later the total sales alone for the year reached $17,028,000, representing the value of 283,806,000 pounds, and total production (for which no value figures are available) reached 366,442,000 pounds. The Bureau of Mines, which publishes annual figures on carbon black, also records an increase in 1930 (despite the slowing down of industry) to 379,942,000 pounds, although the 1931 output dropped to 280,907,000 pounds. Total sales in 1931 stood at 258,426,000 pounds valued at $8,621,000—a drop in average value to about 3 cents per pound as against 5 to 6.5 cents before the depression.

No recent returns are available for bone black and carbon black, but in 1929 the returns showed that the output of both was about the same as for several years before. Bone black in that year showed a production of 54,277,000 pounds valued at $2,490,000 and lampblack 10,765,000 pounds valued at $1,185,000. In 1914 bone black was valued at $1,532,000 and lampblack at $504,000.

Tanning Materials, Natural Dyestuffs, etc.

Grouped together under this heading are a number of materials related to each other by source or the uses to which they are put. They include tanning materials, natural (but not synthetic) dyestuffs, mordants and assistants, and sizes.

This group, of which tanning materials and sizes are the chief constituents, presents an exception to the usual rule of enormous expansion in the year since the war. As indicated by the census figures, it reached its highest point of production immediately after the war in 1919 when the total value of its products was reported at $53,744,000. This was far above the 1929 figure of $39,836,000, and more than twice that of 1931, when output fell to $25,832,000. The latter total is but little higher than the pre-war figure, which in 1914 stood at $20,620,000. In the decade following the war, the value of the output of these industries remained for the most part near $35,000,000.

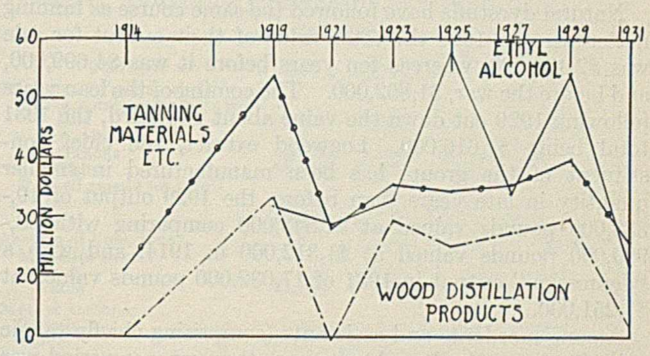


Figure 1. Manufacture of Tanning Materials, Dyes, etc., Wood Distillation Products and Ethyl Alcohol 1914 to 1931

A glance at the detailed returns shows that the lower levels in recent years were due not only to lower prices but to decreased volume as compared with production in the early post-war years. Tanning materials, excluding those made and consumed in the same plant, were valued at $9,958,000 in 1929, less than for any preceding census year since the war and only a third of the heavy output of 1919, when the momentum of war manufacture sent the total up to $32,615,000. In 1931 a production of $7,827,000 was reported. The ravages of chestnut blight and the progressive melting away of the once fine stand of chestnut throughout the east are reflected in the fluctuations, tending gradually downward, of the output of chestnut extract. In 1919 chestnut and oak extracts taken together totaled 507,906,000 pounds; but, since oak extracts account for only some 10,000,000 pounds a year, that figure may be taken as indicating practically the output of chestnut extract following the war. In 1921 chestnut liquid and solid extract aggregated 250,263,000 pounds; in 1923, 433,511,000 pounds; in 1925, 294,424,000 pounds; in

1927, 309,678,000 pounds; and in 1929, 270,162,000 pounds. Preliminary figures for 1931 give the total production as 227,539,000 pounds. The average valuation remains fairly constant around 1.5 cents per pound, about the same as in pre-war years, contrasting with a 1919 valuation of 3.5 cents.

Quebracho extract, for which separate returns have been made only since 1921, likewise shows no consistent gains in the last decade. In that year a production of 65,564,000 pounds (liquid extract) was recorded. In 1931 preliminary figures give the output as 78,586,000 pounds, and, in the years between, the total has fluctuated around 100,000,000 pounds. The average valuation has shown a slight progressive decrease from nearly 4 cents per pound in 1921 to a little more than 2 cents in 1931, so that the total value in 1931 ($1,941,000) was considerably below that of ten years before ($2,447,000). In 1929, 100,067,000 pounds (liquid) valued at $3,229,000 were produced. The growing use of sumac is reflected in the 1931 figures of 5,809,000 pounds valued at $370,000, which compared with 5,279,000 pounds valued at $344,000 in 1929. The increase, however, does not signify any permanent enlargement of this branch of the tanning materials industry. In 1923 the output of sumac extract totaled 6,112,000 pounds, and as long ago as 1914 it was 4,512,000 pounds. Other tanning materials, including chrome tannage, have likewise shown merely up-and-down fluctuations instead of a general upward climb in production.

Natural dyestuffs have followed the same course as tanning materials. In 1929 the total value of their output for sale was $2,426,000, whereas ten years before it was $4,699,000, and before the war, $1,862,000. The coming of the lean years following 1929 cut down the value about one-third, the 1931 total being $1,616,000. Logwood extract, the chief constituent of the group, has been manufactured in smaller quantity in late years than before, the 1929 output of 19,338,000 pounds valued at $1,843,000 comparing with 28,990,000 pounds valued at $1,312,000 in 1914, and with a "depression" output in 1931 of 17,032,000 pounds valued at $1,251,000.

Among mordants and assistants (comprising chiefly tannic acid, Turkey-red oil, and softeners) the post-war period was likewise one of fluctuations rather than steady gains. The total value of mordants manufactured in the United States in 1929 was $1,173,000, slightly less than in 1919 and 1921. Preliminary figures for 1931 show a sharp falling off to $487,000. Tannic acid makes up about one-half the total. Its value of $504,000 in 1929 was less than that for any other census year since the war except 1921 and 1923, and was little more than twice the value of the 1914 output. No separate returns for 1931 have yet been published. Turkey-red oil reached its highest point of production in 1929, both in volume and in value, with a total of 24,261,000 pounds valued at $2,542,000. This was a gain of about 65 per cent over 1927 and was twice the volume and three times the value of the output of 1914. The first two years of the depression, however, cut the output in half, the 1931 returns showing 12,559,000 pounds valued at $1,198,000. Softeners also reached their top figure in 1929 with 31,613,000 pounds valued at $2,248,000, but were much less affected by the slump, as is shown by the 1931 figures of 29,305,000 pounds valued at $1,708,000.

Production of sizes, which had shown a healthy growth after the war, was likewise cut in half in the first two years of the depression. In 1929 the value of output was $13,164,000 and in 1931 only $7,169,000. These figures compare with $11,579,000 for 1919 and $3,053,000 for 1914. The leading article of this group is rosin sizes, which have shown great gains since the war. The 1929 figures of 201,290,000 pounds valued at $6,108,000 compare with 57,056,000 pounds valued at $2,889,000 in 1919 and 20,717,000 pounds at $373,000 in 1914. The preliminary returns for 1931 lump the rosin sizes with other gum sizes, the total for all being 163,752,000 pounds valued at $3,934,000 as against 221,428,000 pounds at $7,509,000 in 1929. Dextrin sizes dropped off in about the same proportion, the 1931 production being valued at $1,135,000 as against $2,043,000 in 1929; sizes of starch, glue, etc., fell from $3,612,000 to $2,100,000, not far from the 1914 level of $1,769,000.

RAYON

Seldom has any industry in peace times shot up to major proportions as swiftly as that of the manufacture of rayon.

Although the new textile had been used since the beginning of the century, it was only after the war that its manufacture really attained the dignity of a separate industry. In 1923 the Bureau of the Census was still including rayon yarn among "chemicals not elsewhere classified," and the amount of total production was not separately stated. In 1925 fourteen establishments, with 19,000 employees and paying $23,000,000 in wages, produced yarn and allied products to a value of $88,061,000, of which yarn totaled 51,902,000 pounds valued at $88,008,000. Two years later nineteen establishments turned out $109,888,000 worth of goods, including 75,555,000 pounds of yarn valued at $106,469,000, and in 1929 the Minerva-like industry reached its high point with twenty-nine establishments, 39,000 employees, an outlay of $44,697,000 in wages, and a total output valued at no less than $149,546,000. Some comparative measure of the heights which the manufacture of this laboratory-born textile had attained in five or six years is to be had in the figures for the manufacture (for sale) of silk threads and yarns, which in 1929 amounted to only $90,342,000 in value.

It was to be expected that the depression would touch this new and popular commodity less drastically than more expensive textiles. In the first two years, at least, such was the case. The early 1931 figures show that although the total value of manufactures of rayon yarn and allied products, such as sheets, straw, etc., dropped off to $132,784,000, or 11.2 per cent less, the quantity of yarns showed an actual increase of 29 per cent over 1929, and two classes returned material gains both in quantity and value. Comparative detailed figures for the two years are given in Table II.

TABLE II. MANUFACTURES OF RAYON YARN AND ALLIED PRODUCTS

	1929	1931[a]
Establishments	29	32
Wage earners (av. for year)	39,106	38,732
Wages	$44,697,000	$38,220,000
Cost of materials, containers for products, fuel, and purchased electric energy	$33,335,000	$36,207,000
Products, total value:	$149,546,000	132,784,000
Yarns:		
Total pounds	116,632,000	150,510,000
Total value	$140,847,000	$112,434,000
Finer than 125 denier:		
Pounds	12,814,000	32,959,000
Value	$21,177,000	$30,525,000
125 to 150 denier:		
Pounds	85,529,000	99,653,000
Value	$101,495,000	$70,877,000
Heavier than 150 denier:		
Pounds	18,290,000	17,897,000
Value	$18,175,000	$11,032,000
Allied products (sheets, waste, etc.), value	$8,700,000	$20,350,000
Value added by manufacture	$116,211,000	$96,577,000

[a] Preliminary figures.

In 1929 Pennsylvania, Virginia, and Tennessee were the three leading states in value of output, but thirteen other states reported varying quantities manufactured, the industry extending as far south as Georgia and as far west as Illinois. Materials used in 1929 included 48,294 tons of wood pulp, valued at $5,410,000; 61,136,000 pounds of cotton linters, valued at $5,844,000; and chemicals valued at $16,897,000.

The above figures apply to the manufacture of rayon yarns, etc., as raw materials for the textile industry. The extent of their use in making various fabrics (including pure rayon textiles and mixtures of rayon with silk, cotton, and wool) is also recorded in census returns. The chief outlets for rayon yarns are knit goods, silk manufacturing, and cotton goods and cotton small wares. For the three census years covering the period of heightened production for which returns are available (1931 figures are not yet published), the use of rayon yarns in these and other industries was as shown in Table III (pure rayon woven goods are included in the figures for the silk industry).

TABLE III. RAYON YARN USED IN VARIOUS INDUSTRIES

(In thousands of pounds)

INDUSTRY	1925	1927	1929
Cotton goods and small wares	15,180	28,361	34,512
Wool manufactures:			
Woolen goods	1,744	735	959
Worsted goods	787	789	2,523
Carpets and rugs	[a]	21	13
Knit goods	23,680	36,581	56,368
Silk manufactures	15,728	23,158	32,552
Lace goods	[a]	[a]	1,362
Total	57,119	89,645	128,289

[a] Not separately stated.

The demands of these industries in 1929 exceeded total yarn production (greatly increased as it was) by some 12,000,000 pounds.

Included in the products of the silk industry in 1929 were all-rayon woven goods amounting to 66,024,000 square yards, valued at $34,738,000, of which Pennsylvania products accounted for $12,964,000, those of New Jersey $5,796,000, and those of North Carolina $5,519,000; goods of silk and rayon mixed, amounting to 31,739,000 square yards valued at $24,428,000, Pennsylvania being credited with 45 and New Jersey with 40 per cent; and goods of rayon and cotton mixed (not including goods made in cotton mills), 37,241,000 square yards valued at $16,617,000, with Pennsylvania, New Jersey, Rhode Island, and several other states prominent in production. The 1929 output of the silk industry also included rayon yarns thrown, twisted, and otherwise further manufactured to a value of $7,803,000; velvets of silk and rayon mixed, $12,887,000; ribbons of silk and rayon mixed, $9,474,000, etc. No 1931 figures are yet available.

Among the more prominent articles of pure rayon or of rayon mixed with other yarns, the knit goods industry reported a total manufacture of pure rayon hosiery and rayon hosiery with cotton tops, heels, and toes (excluding infants' and athletic and golf hose) amounting to 16,501,000 dozen pairs valued at $46,741,000 in 1929 as against 11,541,000 dozen pairs with an approximate value of $28,200,000 in 1927; hosiery of silk and rayon mixed, $20,631,000 in 1929 and $33,254,000 in 1927; hosiery of wool and rayon mixed, $4,684,000 in 1929 and $5,941,000 in 1927; hosiery of cotton and rayon mixed, $32,018,000 in 1929 and $22,428,000 in 1927; rayon underwear, $26,616,000 in 1929 and $23,605,000 in 1927; and rayon tubing, $29,761,000 in 1929 and $20,873,000 in 1927. In the cotton goods industry a 1929 manufacture of fabrics (other than shirtings and draperies) of cotton and rayon mixed (whose chief value was in cotton), valued at $28,984,000, was reported; and of fabrics (except draperies) wholly or in chief value of rayon, $24,161,000. There are no comparable figures for earlier years, and 1931 figures for both the cotton and knit goods industries are yet to be published.

WOOD DISTILLATION AND CHARCOAL MANUFACTURE

As indicated by the preliminary returns from the 1931 census, the depression struck the wood-distillation industry with special severity. The total value of products of the industry (which include hardwood and softwood distillation and the manufacture of charcoal in kilns or pits) dropped 62 per cent in 1931 as compared with 1929, and was little higher than that of twenty-two years before. Including charcoal (and also a small amount of products not especially related to wood-distillation processes), the value of the industry's production in 1931 was $11,153,000, as compared with $29,594,000 in 1929, which figure was about three times the pre-war value.

Taking into account by-products of other industries which are properly to be classified with wood-distillation products, the total value of the latter in 1931 was $11,178,000 and in 1929, $30,289,000. The most precipitate drop among the various commodities manufactured was in crude and refined methanol and acetate of lime, each of which fell off nearly 80 per cent in total value and more than 50 per cent in quantity. Wood tar made for sale declined about three-fourths both in quantity and value, and wood rosin nearly 70 per cent in value. Other decreases were smaller but very marked.

The comparative figures (Table IV) for census years since 1909 indicate the effect of the depression on the production of the chief articles in this group, and show how the industry in general has fallen back to pre-war levels, or, in the case of commodities such as methanol, to much less than before the war.

TABLE IV. OUTPUT OF WOOD-DISTILLATION PRODUCTS IN U. S.

(In thousands)

PRODUCT	1909	1914	Av. 1919–27	1929	1931[a]
Methanol (wood alcohol):					
Crude, total production, gallons	9,308	9,602	7,770	8,355	4,136
For sale:					
Gallons	6,773	7,197	5,778	5,101	2,185
Value	$1,774	$1,606	$2,982	$1,794	$383
Refined (made for sale):					
Gallons	6,733	6,235	5,122	6,676	2,760
Value	$3,097	$2,709	$4,275	$3,907	$851
Acetate of lime, tons	[b]	83	71	65	[b]
Made for sale:					
Tons	71	82	64	58	26
Value	$2,118	$2,139	$3,128	$4,695	$973
Methyl acetone:					
Pounds	[b]	[b]	2,826	4,675	3,615
Value	[b]	[b]	$377	$575	$233
Miscellaneous chemicals produced principally from wood distillation products, value	[b]	[b]	$1,260	$3,841	$1,128
Tar, total production, gallons	[b]	2,965	5,441	10,518	5,488
For sale:					
Gallons	1,570	1,477	3,365	6,904	1,886
Value	$113	$146	$556	$879	$225
Tar oil:					
Gallons	[b]	[b]	1,077	997	859
Value	[b]	[b]	$240	$201	$119
Pitch:					
Pounds	[b]	[b]	23,022[c]	8,587	10,872
Value	[b]	[b]	$352[c]	$102	$94
Turpentine, wood:					
Gallons	707	576	2,417	4,619	3,141
Value	$250	$194	$1,442	$1,714	$1,031
Pine oil:					
Gallons	[b]	[b]	2,062[d]	2,722	2,150
Value	[b]	[b]	$888[d]	$1,272	$1,014
Rosin, wood:					
Barrels (500 pounds)	[b]	29	220	479	334
Value	[b]	$198	$2,584	$5,443	$1,905
Charcoal (made for sale):					
Bushels	39,952	44,828	38,953[e]	45,355	22,170
Value	$2,427	$2,830	$6,404[e]	$5,473	$3,031

[a] Preliminary figures. [b] No data available. [c] Average 1925–27. [d] Average 1923–27. [e] Average 1921–27.

No statistics are available to show what proportion of these products came from hardwood distillation and what from softwood, except in the case of charcoal. In 1929, out of a total production (for sale) of 45,355,000 bushels valued at $5,473,000 from seventy-six establishments, about 90 per cent (or 40,829,000 bushels valued at $4,923,000) came from the fifty-two hardwood distillation concerns. A somewhat larger proportion was recorded in 1925 and 1927.

There has been a general tendency in the wood-distillation and charcoal industries to concentrate into fewer and larger plants. In 1923 the 123 establishments reported employed an average of 4123 wage earners for the year and had a plant capacity of 14,910 horsepower. In 1929 ninety-one establishments employed an average of 4648 workers and had the use of 25,509 horsepower. The 1931 returns showed a drop to sixty-four establishments and to a pay roll of 2617 workers. Of the 1929 establishments fifty-five were engaged in hardwood distillation, twenty-five in softwood, and eleven in the manufacture of charcoal in pits and kilns in which the volatile constituents of the wood were not recovered. Further facts relating to the branches represented in this group of manufactures are shown in Table V.

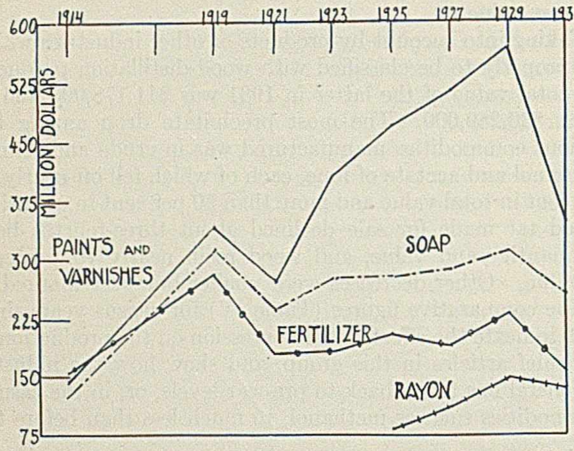


FIGURE 2. MANUFACTURE OF PAINTS AND VARNISHES, SOAP, FERTILIZER, AND RAYON 1914 TO 1931

TABLE V. WOOD DISTILLATION AND CHARCOAL MANUFACTURE

	HARDWOOD DISTILLATION		SOFTWOOD DISTILLATION		CHARCOAL MANUFACTURE	
	1927	1929	1927	1929	1927	1929
Establishments	57	55	19	25	12	11
Wage earners (av. for year)	2,898	2,838	1,535	1,752	104	58
Wages (in thousands)	\$3,249	\$3,442	\$1,380	\$1,789	\$110	\$63
Horsepower (rated capacity)	9,755	17,510	6,793	7,897	285	102
Value of products[a] (in thousands)	\$17,414	\$19,478	\$9,800	\$9,842	\$416	\$274
Value added by manufacture (in thousands)	\$6,593	\$8,532	\$5,418	\$6,078	\$198	\$193

[a] For 1929, manufacturers' sales (shipments or deliveries); for 1927, production.

Among the states for which separate returns were shown in 1929, Michigan led all others in the value of products, followed by New York, Pennsylvania, and Tennessee.

ETHYL ALCOHOL AND DISTILLED LIQUORS

Following the advent of national prohibition, the manufacture of the three classes of products included in this group—ethyl alcohol (pure or denatured), whiskey, and nonbeverage rum—as given in census returns, dropped to about 15 per cent of their pre-war value. In the years since 1919 this yield has fluctuated considerably, reaching in 1925 and 1929 a value more than one-fourth the pre-war figure. In 1931 it dropped back to the lowest level since the war, 60 per cent less than in 1929. Actual figures showing the value of production in census years before and after the coming of prohibition are given in Table VI.

Only a few states are shown separately in the returns. Of those mentioned in 1929, Louisiana was well in the lead with an output valued at \$13,593,000. This was more than twice as much as for 1927. Pennsylvania was a good second with \$12,616,000, three times as much as in 1927. Manufacture in these states was carried on in a few large plants, the average number of wage earners in 1929 for the whole state of Louisiana being only 342 and for Pennsylvania 302.

TABLE VI. MANUFACTURE OF ETHYL ALCOHOL AND DISTILLED LIQUORS

YEAR	ESTABLISHMENTS	WAGE EARNERS[a]	WAGES	VALUE OF PRODUCTS
			Thousands	*Thousands*
1909	613	6430	\$3074	\$204,699
1914	434	6295	3994	206,779
1919	34	1380	1717	31,854
1921	33	1141	1627	28,789
1923	30	1062	1474	33,000
1925	31	1395	1838	57,706
1927	28	1180	1705	33,971
1929[b]	30	1484	2131	54,285
1931[c]	27	977	1331	21,710

[a] Av. for year. [b] Manufacturers' sales (shipments or deliveries). [c] Preliminary figures.

SOAP

One of the oldest of chemical industries—soap making—had become so well stabilized that neither the abnormal boom conditions preceding 1929 nor the abnormal dullness which followed that year affected it as much as most other industries. Actual production in 1931 was only 18 per cent less in value than in 1929, and the 1929 production was only about 10 per cent higher than the average for the preceding decade. That average, owing in part to a higher range of prices, was some two and a half times the pre-war annual value. The record of production in the industry in the last quarter-century is given in Table VII.

TABLE VII. PRODUCTION IN SOAP INDUSTRY

CENSUS YEAR	VALUE OF PRODUCTS	CENSUS YEAR	VALUE OF PRODUCTS
	Thousands		*Thousands*
1909	\$111,358	1925	\$278,273
1914	127,942	1927	287,060
1919	316,740	1929[a]	310,192
1921	240,195	1931[b]	254,164
1923	276,403		

[a] Sales (shipments or deliveries) by manufacturers.
[b] Preliminary figures.

Production in 1929 was thus less than ten years before, and production in 1931, despite the depression, exceeded in value that of 1921 and was twice that of pre-war manufacture. The 1931 decrease in quantity was much less than that in value, and in some instances there were even considerable increases in amount of manufacture. Although money returns in the industry were dropping off 18 per cent, the number of wage earners was declining only 4.2 per cent, the average number for the whole industry in 1931 being reported as 13,762 as compared with 14,363 in 1929. Total wages paid showed a correspondingly small decline, amounting to \$17,330,000 in 1931 and \$18,995,000 in 1929, a drop of 8.8 per cent.

Glancing at the returns for the various classes of soap manufactured, we find that the depression affected the industry very irregularly. In one category, for example, there was a decrease in business of 50 per cent, whereas in two or three others there were actually substantial increases. Although these may be due in part to the fact that 1929 figures represented sales and those for 1931 manufactures, the gains stand out in strong contrast to the returns from nearly all other branches of manufacture.

Hard soaps are the chief soap product, comprising about two-thirds of the total value. They fell from \$199,856,000 in 1929 to \$153,788,000 in 1931, or nearly a fourth, although the quantity dropped only from 2,250,663,000 to 2,098,970,000 pounds, or about 10 per cent. Of these hard soaps, toilet soap suffered only a comparatively light decrease, from 324,384,000 pounds valued at \$59,983,000 to 301,266,000 pounds valued at \$52,614,000. White laundry soap (made from vegetable oils, etc.) fell rather sharply from a valuation of $51,175,000 to $33,221,000, and yellow laundry soap from $40,774,000 to $33,968,000. Soap chips and flakes (also a hard soap item) registered a 28 per cent decrease in value, dropping from $41,764,000 to $30,147,000.

Of the other classes of manufacture besides hard soaps, three grades, including granulated and powdered soap, shaving soap, cream, and powder, and soap stock, all showed increases in value in 1931 over 1929. Granulated and powdered soap enjoyed an output of 414,447,000 pounds valued at $40,283,000 as compared with 337,291,000 pounds valued at $35,725,000 in 1929. Shaving soap, cream, and powder were manufactured to a value of $11,176,000 as compared with $10,794,000, and soap stock or base to a value of $522,000 as compared with $292,000. Soap powders, liquid soap, paste soap, and soft soap showed decreases, respectively, of 23, 40, 38, and 50 per cent.

FERTILIZERS

With the principal farm products returning unprecedentedly low prices, it was inevitable that the general slump should extend itself in full force to commercial fertilizers. Returns just released by the Government show that the total value of the products of fertilizer manufacturers in 1931 was $155,151,000 as against $232,511,000 in 1929, a drop of 33 per cent. The new figure is but little more than half that of 1919 and is practically the same as the pre-war 1914 total. Leaving out of account the nonfertilizer products of fertilizer plants and adding fertilizer made as by-products in other industries, we find that the total actual fertilizer manufactured in 1931 was valued at $141,111,000 as against $222,731,000 in 1929.

As classified by the census, this industry covers only the manufacture of commercial fertilizers, the two chief classes of which are so-called complete fertilizers (mixtures of superphosphates, potash, and ammoniates) and superphosphates, and does not include tankage and other materials used in their natural state. Details of production in the last two census years are given in Table VIII.

Entering into the composition of complete fertilizer are: a number of nitrogen compounds, chiefly nitrate of soda; potash salts; superphosphates; cottonseed meal, tankage, fish scrap, etc.; sulfur, sulfuric acid, and ammonium sulfate. The latest returns showing amounts of these materials used in the fertilizer industry are for 1929. Some of the more important items for that year compared to 1919, when the industry registered its greatest production with output valued at $281,000,000, are as follows: Sulfuric acid, 1,373,000 tons (50° Bé.) made and consumed and 922,000 purchased in 1929, as against 1,569,000 and 637,000 in 1919 (fertilizer companies on the average make about one-fourth of the country's total of sulfuric acid each year); phosphate rock, 2,291,000 tons in 1929 and 2,247,000 in 1919; superphosphates (basis 20 per cent or less, run of pile) made and consumed in the same establishment, 1,602,000 tons in 1929 and 3,316,000 in 1919; other superphosphates, 1,368,000 tons in 1929 and 1,200,000 in 1919; nitrate of soda, 240,000 tons in 1929 and 152,000 in 1919; sulfate of ammonia, 461,000 tons in 1929 and 136,000 in 1919; sulfur, 339,000 tons in 1929 and 222,000 in 1919; pyrites, 201,000 tons in 1929 and 399,000 in 1919.

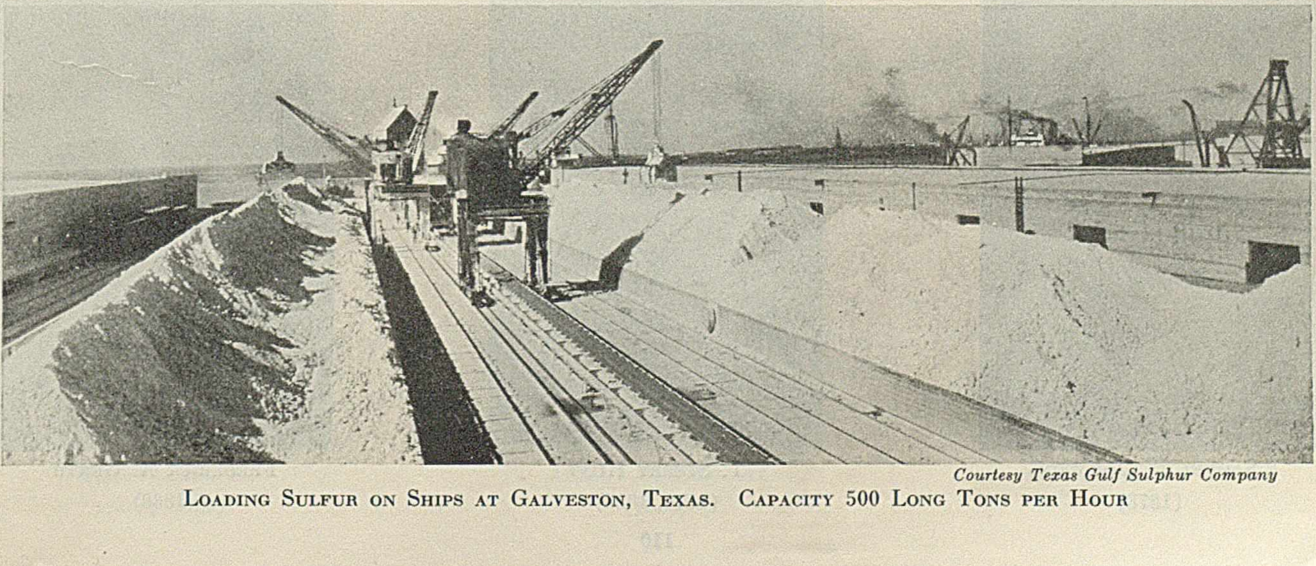
TABLE VIII. MANUFACTURE OF COMMERCIAL FERTILIZER

	1929	1931[a]
Establishments	638	590
Wage earners	20,926	14,803
Wages	$17,884,000	$12,314,000
Products, total value	$232,511,000	$155,151,000
Fertilizer	$201,751,000	$134,990,000
Other products	$30,760,000	$20,161,000
Total fertilizer made in U. S.	$222,731,000	$141,111,000
Fertilizer industry	$201,751,000	$134,990,000
Other industries	$20,980,000	$6,121,000
Complete fertilizer:		
Tons	5,992,000	4,548,000
Value	$168,838,000	$110,819,000
Superphosphates (including concentrated phosphates), total production, tons	4,133,000	3,522,000[b]
For sale:		
Tons	2,531,000[b]	1,997,000[b]
Value	$28,375,000	$21,048,000
Made and consumed, tons	1,602,000[c]	1,525,000[b]
Potash superphosphates:		
Tons	211,000	146,000
Value	$4,854,000	$2,964,000
Fish scrap:		
Tons	85,000	44,000
Value	$3,245,000	$1,368,000
Bone meal:		
Tons	40,000	35,000
Value	$1,544,000	$927,000
Other fertilizer:		
Tons	462,000	189,000
Value	$15,874,000	$3,984,000

[a] Preliminary figures. [b] Basis of 16 per cent available phosphoric acid.
[c] Basis of 20 per cent or less phosphoric acid, run of pile.

Out of a total value in 1929 of $222,731,000 the leading state in point of value of fertilizer production was Georgia, with $26,734,000; North Carolina was second, with $22,146,000. Other leading states include the following: Maryland, $19,707,000 (led all other states in quantity of production, with 1,208,000 tons); Virginia, $19,252,000; Florida, $14,963,000; New Jersey, $13,641,000; Ohio, $12,800,000; and Alabama, $12,182,000.

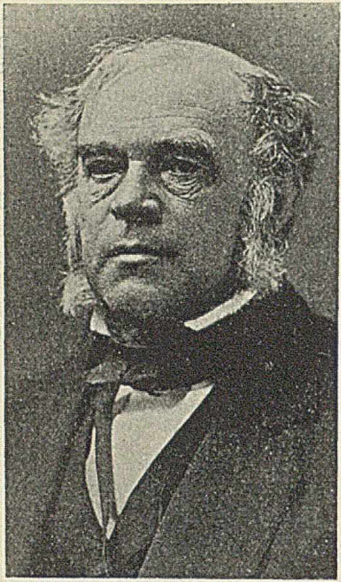
RECEIVED November 9, 1932.



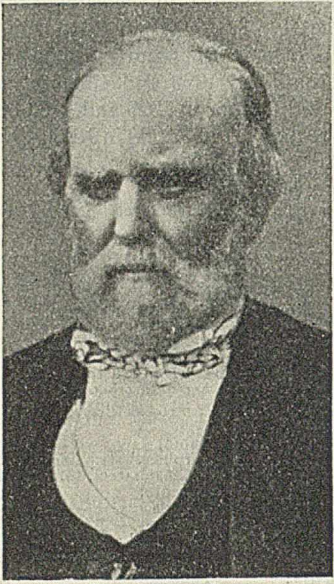
Courtesy Texas Gulf Sulphur Company

LOADING SULFUR ON SHIPS AT GALVESTON, TEXAS. CAPACITY 500 LONG TONS PER HOUR

Presidents of the American



John W. Draper
(1876)



J. Lawrence Smith
(1877)

IF POPE, the British poet, not the chemist, is correct in saying, "The proper study of mankind is Man," then the men who, as presidents, have been leaders of the American Chemical Society should furnish an interesting and worthwhile study.

Association with this noteworthy group in the preparation of this paper has been an inspiration. Almost without exception they possess a wonderful capacity for work, and this work lies in widely different fields—from that of practical usefulness to abstruse theory, from the invention of the ink used to print greenback currency and of the flush water-closet (left unpatented so that its general use might bring an improvement in sanitary conditions) to outstanding studies on atomic weights, on the structure of the atom, and of the most complex compounds.

It was a prolific group chemically, the published papers being estimated at four or five thousand, and the books, usually on chemistry but some on a wide variety of subjects, at several hundred.

These presidents include the "chemist of the Confederacy" as well as an assistant surgeon in the Union Army and another Union soldier who was wounded. Half a dozen were actively engaged in the World War.

Table I gives a list of these men with certain facts in the life of each. This information has come from many sources, the most important of which are given under references at the close of the paper.

Of the forty-five presidents, two served three terms—Booth consecutively from 1883–5, and Edgar F. Smith, who after his first term in 1895 was again elected for 1921 and for 1922. Nine served two terms—Hunt in 1879 and 1888, Chandler in 1881 and 1889, and the other seven two consecutive years. Thirty-four were in office the usual one year.

Longevity

The average age of the presidents of the Society has been 55, the youngest being Arthur A. Noyes at 38 and the oldest J. C. Booth, serving three terms from 73 to 75. The age

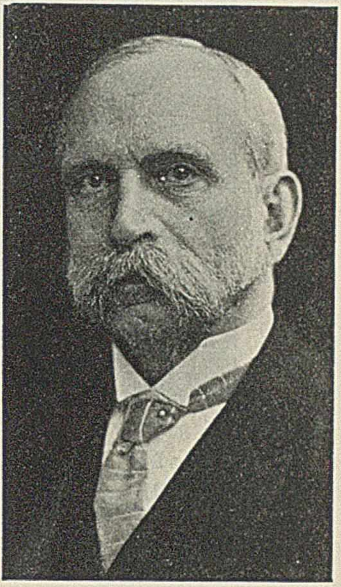
Samuel W. Johnson
(1878)

T. Sterry Hunt
(1879, 1888)

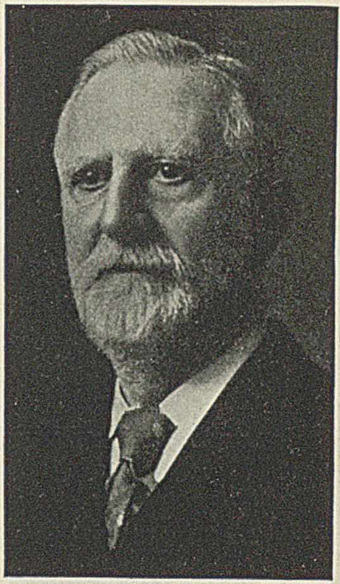
Frederick A. Genth
(1880)

Chemical Society

HARRISON HALE AND EDNA LUCILE NELSON
University of Arkansas
Fayetteville, Ark.



CHARLES F. CHANDLER
(1881, 1889)



JOHN W. MALLET
(1882)

average in the first thirty years of the SOCIETY's history is practically identical with that since 1905. The average age of Presidents of the United States at inauguration is only one year less, or 54.

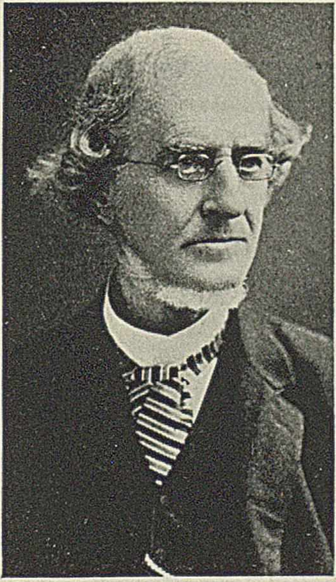
The traditional belief that chemists, in spite of laboratory fumes and supposed professional dangers, live long is confirmed by this group. Of the twenty-six now dead the average life was 73 (of the Presidents of the United States, 68), the shortest life being the 57 years of Alexander Smith and the longest that of Charles F. Chandler at 89. H. W. Wiley lived 86 years, E. W. Morley 85, and F. W. Clarke 84. The average age of the nineteen now living is 65 with the distinction of seniority being held by Charles E. Munroe at 83; he is also the only surviving charter member of the SOCIETY.

BIRTHPLACE

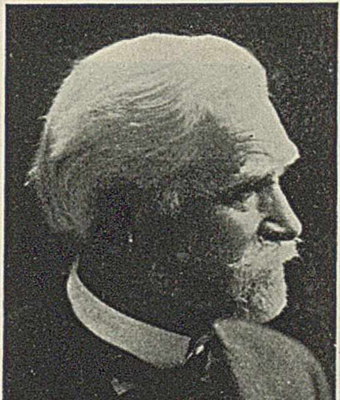
Most interesting is the wide geographical distribution of the birthplaces of this group. Nine of the forty-five were born abroad, four of whom served in the first thirty years of the SOCIETY's life and five in the remaining twenty-eight. A glance at Table II shows a wider distribution since 1905. In the first period two foreign countries and nine states furnished twenty-four men; in the second period twenty-one men came from five foreign countries and twelve states. Massachusetts with nine and New York with eight have been the most prolific in chemical presidents.

Not until 1920 did the AMERICAN CHEMICAL SOCIETY have a president born west of the Mississippi River; it took the American nation eight years to follow the lead of our SOCIETY and elect a President of the United States from this area. Iowa furnished W. A. Noyes to the SOCIETY and also Herbert Hoover to the nation. Only one other of our chemical presidents may be so classified—E. C. Franklin of Kansas, later of California.

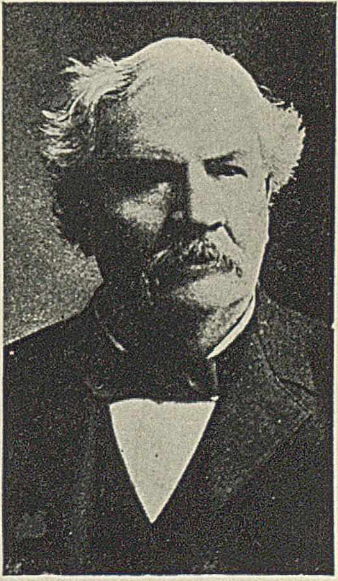
That this has not been due to prejudice but only to the different ages of the sections seems evident, for apparently the SOCIETY has been singularly free from sectionalism. It



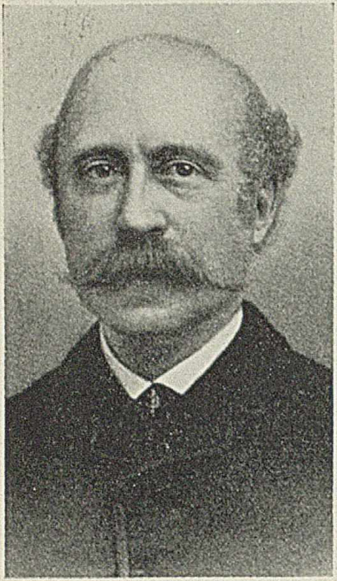
JAMES C. BOOTH
(1883–1885)

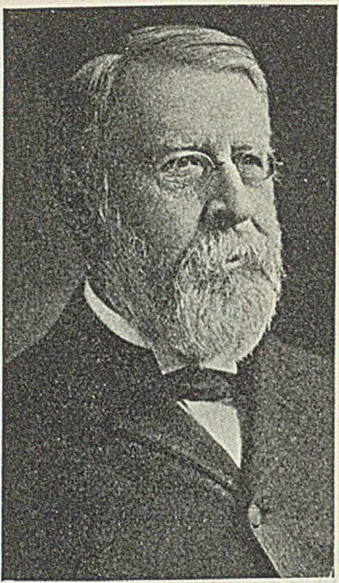


ALBERT B. PRESCOTT
(1886)



CHARLES A. GOESSMANN
(1887)





Reading from left to right:

Henry B. Nason
(1890)

George F. Barker
(1891)

George C. Caldwell
(1892)

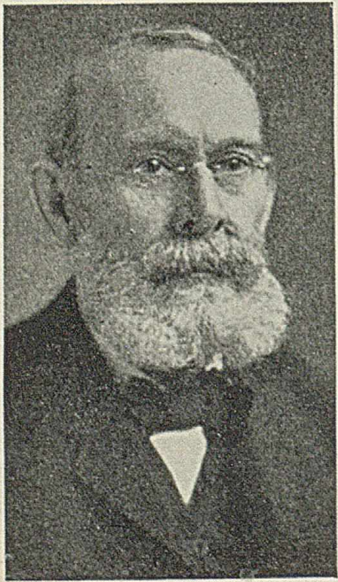
Harvey W. Wiley
(1893, 1894)

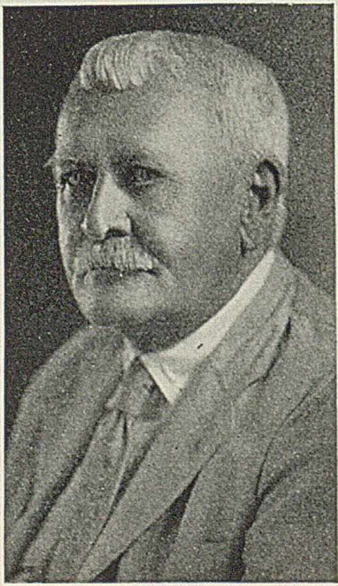
Edgar Fahs Smith
(1895, 1921, 1922)

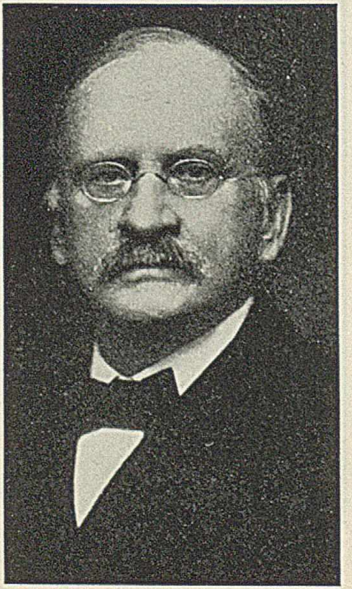
Charles B. Dudley
(1896, 1897)

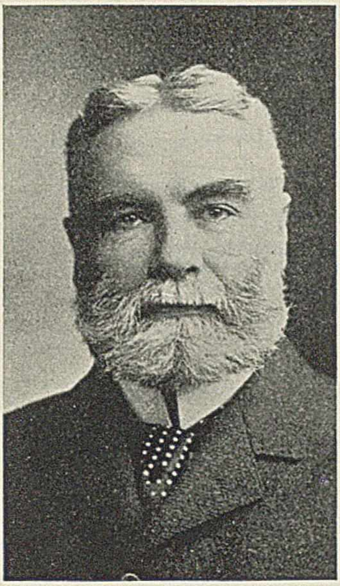
Charles E. Munroe
(1898)

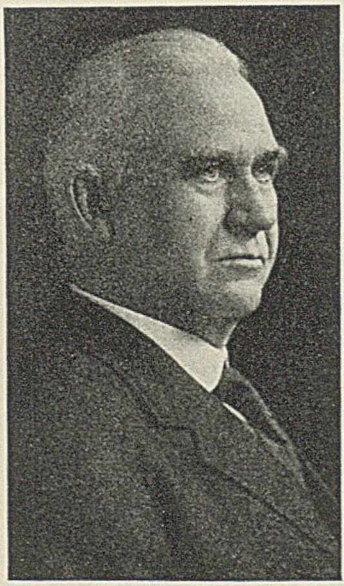
Edward W. Morley
(1899)









Reading from left to right:
William McMurtrie
(1900)
Frank Wigglesworth Clarke
(1901)
Ira Remsen
(1902)
John H. Long
(1903)
Arthur A. Noyes
(1904)
Francis P. Venable
(1905)
William F. Hillebrand
(1906)
Marston T. Bogert
(1907, 1908)

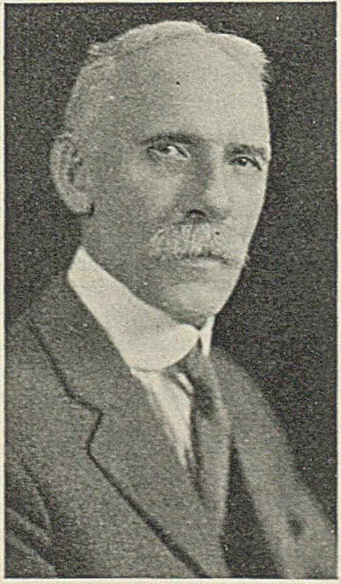
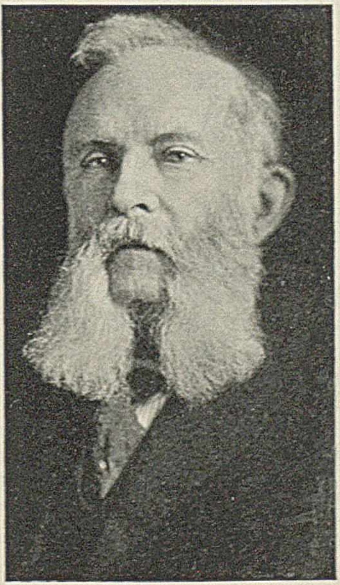





TABLE I. STATISTICS ON PRESIDENTS

No.	Year	Name	Dates of Birth-Death	Birthplace	Education
1	1876	John William Draper[a]	1811–1882	St. Helen's near Liverpool, England (came to U. S. 1832)	London Univ.; M.D., Pennsylvania, '36
2	1877	John Lawrence Smith[a]	1818–1883	Charleston, S. C.	M.D., South Carolina, '40; Paris; Giessen
3	1878	Samuel William Johnson	1830–1909	Kingsborough, N. Y.	Yale; Leipzig; Munich; Giessen
4	1879	Thomas Sterry Hunt[a]	1826–1892	Norwich, Conn.	Yale
5	1880	Frederick Augustus Genth[a]	1820–1893	Wachsterbach, near Hanau, Germany (came to U. S. 1848)	Heidelberg; Giessen; Ph.D., Marburg, '45
6	1881	Charles Frederick Chandler[a]	1836–1925	Lancaster, Mass.	Harvard; Berlin; Ph.D., Gottingen, '56
7	1882	John William Mallet[a]	1832–1912	Dublin, Ireland (came to U. S. 1853)	A.B., Trinity; Ph.D., Gottingen, '52
8	1883–5	James Curtis Booth	1810–1888	Philadelphia, Pa.	A.B., Pennsylvania, '29; Cassel; Berlin
9	1886	Albert Benjamin Prescott[a]	1832–1905	Hastings, N. Y.	M.D., Michigan, '64
10	1887	Charles Anthony Goessmann[a]	1827–1910	Naumburg, Germany (came to U. S. 1857)	Ph.D., Gottingen, '53
	1888	Thomas Sterry Hunt	(See No. 4)	....	....
	1889	Charles Frederick Chandler	(See No. 6)	....	....
11	1890	Henry Bradford Nason[a]	1831–1895	Foxborough, Mass.	A.B., Amherst, '55; Ph.D., Gottingen, '57
12	1891	George Frederick Barker[a]	1835–1910	Charlestown, Mass.	Ph.B., Yale, '58
13	1892	George Chapman Caldwell	1834–1907	Framingham, Mass.	B.S., Harvard, '55; Ph.D., Gottingen, '57
14	1893–4	Harvey Washington Wiley	1844–1930	Kent, Ind.	A.B., Hanover, '67; A.M., Hanover, '70; M.D., Ind. Medical, '71
15	1895	Edgar Fahs Smith	1854–1928	York, Pa.	B.S., Pennsylvania Coll., '74; Ph.D., Gottingen, '76
16	1896–7	Charles Benjamin Dudley	1842–1909	Oxford, N. Y.	A.B., Yale, '71; Ph.D., Yale, '74
17	1898	Charles Edward Munroe[a]	1849–	Cambridge, Mass.	B.S., Harvard, '71; Ph.D., George Washington, '94
18	1899	Edward William Morley	1838–1923	Newark, N. J.	A.B., Williams, '60; A.M., Williams, '65
19	1900	William McMurtrie[a]	1851–1913	Belvidere, N. J.	E.M., Lafayette, '71; M.S., Lafayette, '74; Ph.D., Lafayette, '75
20	1901	Frank Wigglesworth Clarke	1847–1931	Boston, Mass.	B.S., Harvard, '67
21	1902	Ira Remsen	1846–1927	New York, N. Y.	A.B., C. C. N. Y., '65; M.D., Columbia, '67; Ph.D., Gottingen, '70
22	1903	John Harper Long	1856–1918	Steubenville, Ohio	B.S., Kansas, '77; Sc.D., Tubingen, '79; Wurzburg; Breslau
23	1904	Arthur Amos Noyes	1866–	Newburyport, Mass.	S.B., M. I. T., '86; M.S., M. I. T., '87; Ph.D., Leipzig, '90
24	1905	Francis Preston Venable	1856–	Prince Edward County, Va.	A.B., Virginia, '78; A.M., Virginia, '79; Bonn; Ph.D., Gottingen, '81; Berlin
25	1906	William Francis Hillebrand	1853–1925	Honolulu, Hawaii	Cornell; Ph.D., Heidelberg, '75; Strasbourg; Freiburg
26	1907–8	Marston Taylor Bogert	1868–	Flushing, N. Y.	A.B., Columbia, '90; Ph.B., Columbia, '94
27	1909	Willis Rodney Whitney	1868–	Jamestown, N. Y.	B.S., M. I. T., '90; Ph.D., Leipzig, '06
28	1910	Wilder Dwight Bancroft	1867–	Middletown, R. I.	A.B., Harvard, '88; Ph.D., Leipzig, '92
29	1911	Alexander Smith	1865–1922	Edinburgh, Scotland (came to U. S. 1890)	B.S., Edinburgh, '86; Ph.D., Munich, '89
30	1912–3	Arthur Dehon Little	1863–	Boston, Mass.	M. I. T.
31	1914	Theodore William Richards	1868–1928	Germantown, Pa.	B.S., Haverford, '85; A.B., Harvard, '86; Ph.D., Harvard, '88; Gottingen
32	1915–6	Charles Holmes Herty	1867–	Milledgeville, Ga.	Ph.B., Georgia, '86; Ph.D., Hopkins, '90; Berlin; Zurich
33	1917	Julius Oscar Stieglitz	1867–	Hoboken, N. J.	Realgymn., Karlsruhe; Ph.D., Berlin, '89
34	1918–9	William Henry Nichols	1852–1930	Brooklyn, N. Y.	B.S., N. Y. U., '70; M.S., N. Y. U., '73
35	1920	William Albert Noyes	1857–	Independence, Iowa	A.B., Grinnell, '79; Ph.D., Hopkins, '82
	1921–2	Edgar Fahs Smith	(See No. 15)	....	....
36	1923	Edward Curtis Franklin	1862–	Geary City, Kans.	B.S., Kansas, '88; M.S., Kansas, '90; Berlin; Ph.D., Hopkins, '94
37	1924	Leo Hendrik Baekeland	1863–	Ghent, Belgium (came to U. S. 1889)	B.S., Ghent, '82; Sc.D., Ghent, '84
38	1925–6	James Flack Norris	1871–	Baltimore, Md.	A.B., Hopkins, '92; Ph.D., Hopkins, '95
39	1927	George David Rosengarten	1869–	Philadelphia, Pa.	B.S., Pennsylvania, '90; Ph.D., Jena, '92
40	1928	Samuel Wilson Parr	1857–1931	Granville, Ill.	B.S., Illinois, '84; M.S., Cornell, '85; Berlin; Zurich
41	1929	Irving Langmuir	1881–	Brooklyn, N. Y.	Met.E., Columbia, '03; Ph.D., Gottingen, '06
42	1930	William McPherson	1864–	Xenia, Ohio	B.S., Ohio State, '87; M.S., Ohio State, '90; Sc.D., Ohio State, '95; Ph.D., Chicago, '99
43	1931	Moses Gomberg	1866–	Elizabetgrad, Russia (came to U. S. about 1885)	B.S., Michigan, '90; M.S., Michigan, '92; Sc.D., Michigan, '94; Munich; Heidelberg
44	1932	Lawrence V. Redman	1880–	Oil Springs, Ontario, Canada (came to U. S. 1910)	B.S., Toronto, '08; Kansas
45	1933	Arthur Becket Lamb	1880–	Attleboro, Mass.	A.B., Tufts, 1900; A.M., Harvard, '03; Ph.D., Harvard, '04; Leipzig; Heidelberg

[a] Charter member, A. C. S.

was natural that, since the SOCIETY was founded in New York, its first president should live there. Two of its first vice presidents, each of whom later became president, were from the South, although this was early in the second decade following the Civil War.

This is the more noteworthy since no meeting except those in New York City was held until 1890, and even then the New York monthly meetings continued for three years more. It is well to remember that the character of the SOCIETY began to change rapidly in the early nineties; prior to this the meetings were localized and the membership was three hundred or less. Doubtless an important factor in causing this absence of sectional feeling was and is the fact that so many men have been born in one section of the country, trained in another, and perhaps spent life in a third.

TRAINING

Nine, or 20 per cent, of the presidents were born abroad, coming to America as young men from Canada, England, Ireland, Scotland, Belgium, Russia, and Germany. Not only were 20 per cent born abroad, but thirty-one of the total forty-five studied abroad. The percentage of those studying abroad seems to have varied little, being 67 per cent prior to 1905 and 71 per cent since.

Twenty-three American colleges and universities and five foreign institutions conferred bachelor's degrees upon thirty-nine of these men. Only about a third of the American institutions are state universities. Harvard with seven and Yale with four lead. The degrees of doctor of philosophy were conferred by half a dozen American universities, Johns Hopkins leading with four such degrees. A larger number of German universities conferred more degrees than those conferred in the United States.

All but three of the thirty-one who studied abroad spent some time in Germany. It is well to recognize this debt the SOCIETY owes to certain German universities and especially to individual teachers in these universities. The influence of a man over a particular chemical generation is marked. Thus,

OF THE AMERICAN CHEMICAL SOCIETY

No.	While President			Special Field of Chemistry	Remarks
	Age	Occupation	Residence		
1	65	Teacher	New York, N. Y.	Medical	Pioneer in photography; wrote "History of Conflict between Religion and Science"
2	59	Teacher	Louisville, Ky., Univ. of Louisville	Mineralogical	Method for alkalies; "Peripatetic Philosopher;" collected and studied meteors
3	48	Teacher	New Haven, Conn., Yale Univ.	Agricultural	Established Conn. Agr. Expt. Sta. (first in America); wrote "How Crops Grow"
4	53	Teacher	Boston, Mass.	Mineralogical	Wrote "Systematic Mineralogy"
5	60	Teacher	Philadelphia, Pa., Univ. of Pa.	Mineralogical	Discovered 24 new minerals; cobaltamines with Wolcott Gibbs
6	45	Teacher	New York, N. Y., Columbia Univ.	Industrial	Worked out assay ton weights; "America's first and most distinguished industrial chemist"
7	50	Teacher	Charlottesville, Va., Univ. of Va.	Analytical	Exponent of research; called "chemist of the Confederacy"
8	73–5	Commercial lab.	Philadelphia, Pa.	Analytical	Established first commercial laboratory; polariscope; U. S. Mint, 1848–88
9	54	Teacher	Ann Arbor, Mich., Univ. of Mich.	Organic	Asst. Surgeon U. S. Army, 1864–65; Michigan School of Pharmacy
10	60	Teacher	Amherst, Mass., Mass. Agr. Coll.	Agricultural	Founded Assoc. Official Agr. Chem.
	62	....	....	....	....
	53	....	....	....	....
11	59	Teacher	New York, N. Y., Pratt Inst.	Industrial	Chemist, Standard Oil, 1880–87
12	56	Teacher	Philadelphia, Pa., Univ. of Pa.	Toxicological	Professor of physics; electricity
13	58	Teacher	Ithaca, N. Y., Cornell Univ.	Agricultural	39 years at Cornell
14	49	Govt. chemist	Washington, D. C., U. S. Dept. Agr.	Agricultural	Called "father of Pure Food law"
15	41	Teacher; provost	Philadelphia, Pa., Univ. of Pa.	Analytical	Electroanalysis; atomic weights; history of chemistry
16	54–5	Railroad chemist	Altoona, Pa., Pa. R. R.	Industrial	114th N. Y. Volunteers (wounded); President Am. Soc. for Testing Materials; also Intern. Soc.
17	49	Teacher	Washington, D. C., G. W. Univ.	Industrial	Chairman Com. on Explosives
18	61	Teacher	Cleveland, Ohio, West. Reserve Univ.	Physical	Relative weight of H and of O; work on light with Michelson led to Einstein Theory
19	49	Ind. chemist	New York, N. Y.	Industrial	Chemist, N. Y. Tartar Co.; baking powder
20	54	Govt. chemist	Washington, D. C., U. S. Geol. Survey	Analytical	Chairman Intern. Com. on Atomic Weights
21	56	Teacher	Baltimore, Md., Johns Hopkins Univ.	Organic	Founded *Am. Chem. J.*; strong exponent of research
22	47	Teacher	Chicago, Ill., Northwestern Univ.	Medical	Wrote "Text-Book of Physiological Chemistry"
23	38	Teacher	Boston, Mass., M. I. T.	Analytical	Analysis of rare elements
24	49	Teacher; president of university	Chapel Hill, N. C., Univ. of N. C.	Inorganic	Special work on zirconium
25	53	Govt. chemist	Washington, D. C., U. S. Geol. Survey	Mineralogical	Wrote "Methods of Rock Analysis"
26	39–40	Teacher	New York, N. Y., Columbia Univ.	Organic	Organized Div. Chem. and Chem. Tech., Natl. Research Council; Chem. Warfare Service
27	41	Director of research	Schenectady, N. Y.	Physical	General Electric Co.
28	43	Teacher	Ithaca, N. Y., Cornell	Physical	Editor *J. Phys. Chem.*; Chem. Warfare Service
29	46	Teacher	Chicago, Ill., Univ. Chicago	Physical	Research on sulfur
30	49–50	Indus. lab.	Cambridge, Mass.	Industrial	Engineering chemistry
31	46	Teacher	Cambridge, Mass., Harvard	Analytical	Atomic weights of 28 elements; Nobel Prize
32	48–9	Teacher	Chapel Hill, N. C., Univ. of N. C.	Industrial	Editor IND. ENG. CHEM. 1917–21; new method of turpentine orcharding
33	50	Teacher	Chicago, Ill.	Organic	Chemistry and pharmacy; organic research
34	66–7	Mfg. chemist	New York, N. Y.	Industrial	Allied Chem. & Dye Corp.; President 8th Intern. Congr. Applied Chem.
35	63	Teacher	Urbana, Ill., Univ. of Ill.	Organic	Editor *J. Am. Chem. Soc.*, *Chem. Abstracts*, *Chem. Rev.*, Chem. Monographs
	67–8	....	....	....	....
36	61	Teacher	Stanford Univ., Calif.	Organic	Liquid ammonia as electrolytic solvent
37	61	Chemical mfr.	New York, N. Y.	Industrial	Phenol condensations; Velox; Bakelite
38	54–5	Teacher	Cambridge, Mass., M. I. T.	Organic	Principles organic chemistry; Chem. Warfare Service
39	58	Mfg. chemist	Philadelphia, Pa.	Industrial	Chemical mfr.
40	71	Teacher	Urbana, Ill.; Univ. of Ill.	Industrial	Chemistry of coals; calorimeter; boiler waters; alloys
41	48	Asst. director research	Schenectady, N. Y.	Industrial	A- and N-filled W lamps; atomic hydrogen welding; Nobel Prize
42	66	Teacher; Dean Graduate School	Columbus, Ohio, Ohio State Univ.	Organic	Administrator; Chem. Warfare Service
43	65	Teacher	Ann Arbor, Mich., Univ. of Mich.	Organic	Trivalent carbon; Chem. Warfare Service
44	52	Chemical mfr.	Bloomfield, N. J.	Industrial	Phenol condensations
45	53	Teacher	Cambridge, Mass., Harvard	Physical	Editor, *J. Am. Chem. Soc.*, 1917– ; Director Fixed Nitrogen Research; Chem. Warfare Service

TABLE II. PLACE OF BIRTH

Country or State	Time of Term		Total
	1876–1905	1906–1933	
Great Britain	2	1	3
Germany	2	..	2
Hawaii	..	1	1
Belgium	..	1	1
Russia	..	1	1
Canada	..	1	1
Massachusetts	7	2	9
New York	4	4	8
Pennsylvania	2	2	4
New Jersey	2	1	3
Ohio	1	1	2
Connecticut	1	..	1
Indiana	1	..	1
South Carolina	1	..	1
Virginia	1	..	1
Georgia	..	1	1
Illinois	..	1	1
Iowa	..	1	1
Kansas	..	1	1
Maryland	..	1	1
Rhode Island	..	1	1
Total	24	21	45

Wohler at Cassel for a short time and then at Gottingen for many years taught at least eight men who later became presidents of this SOCIETY; Liebig at Giessen taught three. The universities at Leipzig, Berlin, Munich, and Heidelberg are also outstanding in the training of these and other American chemists.

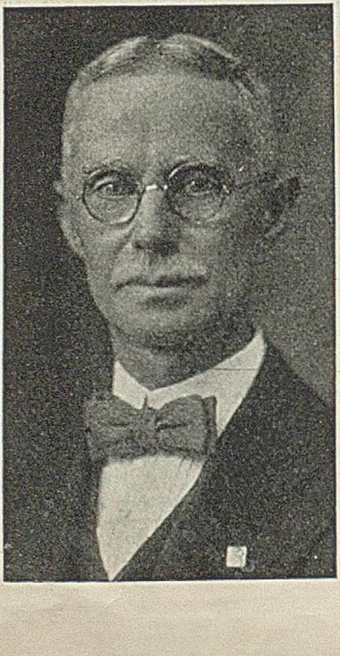
RESIDENCE

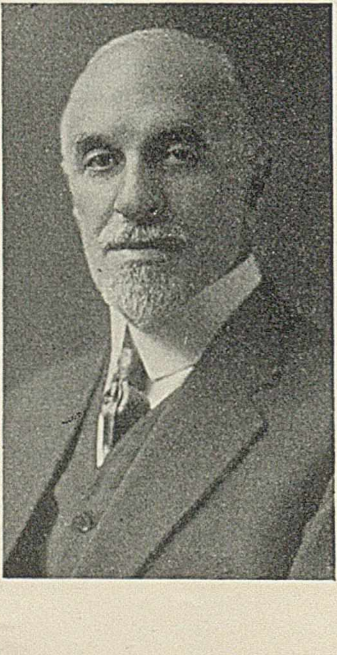
The residence while president is shown in Table III. New York and Massachusetts lead in residence, as they did in birthplace of AMERICAN CHEMICAL SOCIETY presidents, but in reverse order.

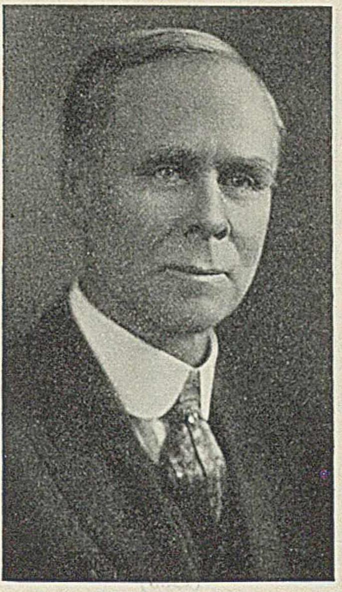
OCCUPATION AND FIELD OF WORK

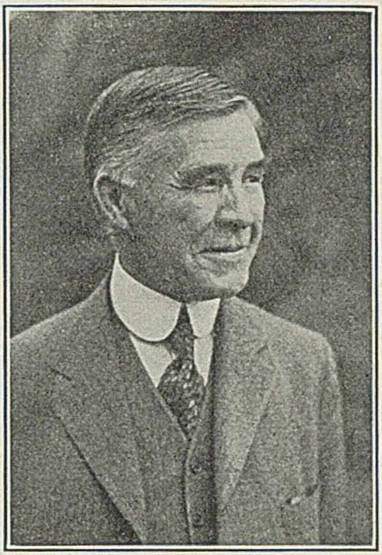
In studying the occupation (Table IV), the number of teachers is impressive. In later years, however, they have not been relatively so numerous. Of all the presidents, 71 per cent have been teachers while president; of those before 1905, 79 per cent were teachers, but only 62 per cent have been since that time. The first seven presidents, and twelve out of the first thirteen, were teachers.

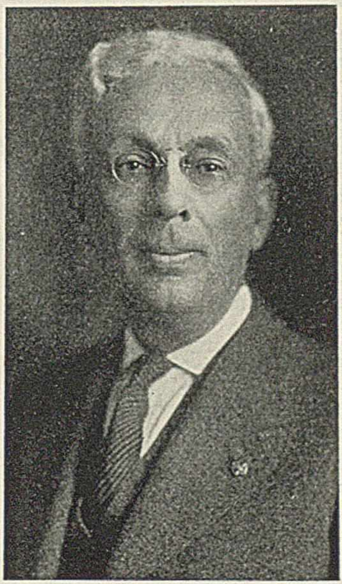
Reading from left to right:
Willis R. Whitney
(1909)
Wilder D. Bancroft
(1910)
Alexander Smith
(1911)
Arthur D. Little
(1912, 1913)
Theodore W. Richards
(1914)
Charles H. Herty
(1915, 1916)
Julius Stieglitz
(1917)
William H. Nichols
(1918, 1919)



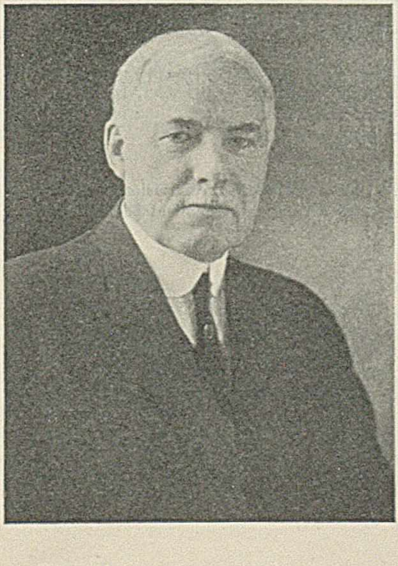


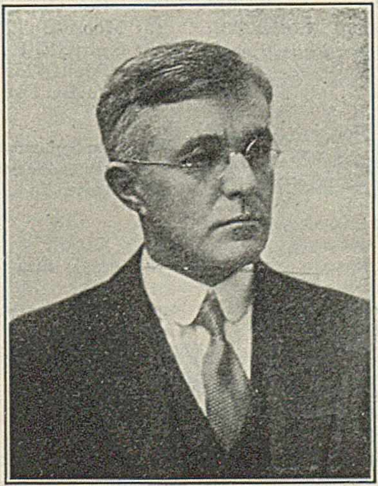




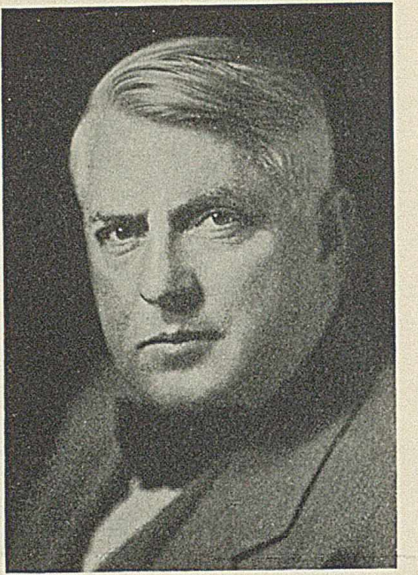


Reading from left to right:
William A. Noyes
(1920)
Edward Curtis Franklin
(1923)
Leo H. Bakeland
(1924)
James F. Norris
(1925, 1926)
George D. Rosengarten
(1927)
Samuel W. Parr
(1928)
Irving Langmuir
(1929)
William McPherson
(1930)





Moses Gomberg
(1931)



L. V. Redman
(1932)

Arthur B. Lamb
(1933)

Table III. Residence while President

State	Time of Term 1876–1905	1906–1933	Total
New York	4	6	10
Massachusetts	3	4	7
Illinois	2	4	6
Pennsylvania	5	1	6
District of Columbia	3	1	4
Michigan	1	1	2
North Carolina	1	1	2
Ohio	1	1	2
Connecticut	1	..	1
Kentucky	1	..	1
Maryland	1	..	1
Virginia	1	..	1
California	..	1	1
New Jersey	..	1	1
Total	24	21	45

Table IV. Occupation

Occupation	Time of Term 1876–1905	1906–1933	Total
Teacher	19	13	32
Commercial laboratory	3	1	4
Manufacturing chemist	..	4	4
Government chemist	2	1	3
Industrial research	..	2	2
Total	24	21	45

Ten of these first thirteen presidents were charter members of the Society. Of the first nineteen presidents (1876–1900) twelve were charter members, and eleven of this twelve were teachers.

The smaller number of teachers holding this office since 1900 shows the increasing number of chemists who are not teachers. Members of the Society seem to have been chemists all, and election has been based upon fitness of those available rather than upon occupation.

The material in Table I under the heading, Special Field of Chemistry, is decidedly questionable. It is impossible to place some men or satisfactorily to limit them to one classification. The data are of interest in showing the increasing number of men in industrial, organic, and physical fields, and the decrease in medical, analytical, mineralogical, and agricultural. Numerous explanations of this change are possible.

It is fully realized that conditions have changed greatly in the fifty-eight years covered by this list, and that the present duties of a president of a society of nearly twenty thousand members in every state and in many foreign countries are by no means the same as those of an early president of a society of three hundred holding monthly meetings in New York City.

Bibliography

(1) American Chemical Society, Directories; Minutes of the Council.

(2) Browne, C. A., "A Half-Century of Chemistry in America, 1876–1926," *J. Am. Chem. Soc.*, 48, No. 8a (1926).

(3) Cattell and Cattell, "American Men of Science," all editions, Science Press, New York.

(4) Encylopedia Americana, Americana Corp., New York and Chicago, 1932.

(5) Johnson and Malone, "Dictionary of American Biography," Scribner, 1928.

(6) *J. Am. Chem. Soc.*, *J. Chem. Education*, Ind. Eng. Chem., Biographical articles and items.

(7) Killeffer, "Eminent American Chemists," D. H. Killeffer, New York, 1924.

(8) Marquis, "Who's Who in America," all editions, A. N. Marquis Co., Chicago.

(9) Moore-Hall, "A History of Chemistry," McGraw-Hill, 1931.

(10) Smith, E. F., "Chemistry in America," Appleton, 1914.

(11) "Twenty-Fifth Anniversary of the American Chemical Society," *J. Am. Chem. Soc.*, Supplement (1902).

Received September 9, 1932. Presented before the Division of History of Chemistry at the 84th Meeting of the American Chemical Society, Denver, Colo., August 22 to 26, 1932.

BOOK REVIEWS

CHEMISTRY TRIUMPHANT. THE RISE AND REIGN OF CHEMISTRY IN A CHEMICAL WORLD. *By William J. Hale.* A Century of Progress Series. 151 pages. The Williams & Wilkins Co., Baltimore, 1932. Price, $1.

The author begins with a discussion of civilization at the chemical threshold and in a series of brief paragraphs describes the fundamental forces which have contributed to what we call modern civilization. The second and third chapters, in which chemistry is introduced more specifically, are evidently not intended to engage the attention of those without some chemical background and some familiarity with chemical terminology. The chemist, however, will find them interesting as a source of concise statements showing the importance of the early discoveries in leading up to a chemical concept.

Then follows in interesting fashion detailed reference to the beginnings of chemical industry, as we now know it, which is introductory to the fifth chapter—The Chemical Revolution. The author depicts this as the second of the great revolutions profoundly affecting world affairs, the first having been the so-called industrial revolution when power and machinery were introduced, late in the eighteenth and early in the nineteenth centuries. According to the author, "The economists of the future will attribute the cause of this second cataclysm to the increasing replacement on a large scale of much of nature's output by direct chemical adaptations springing from the genius and industry of man." Natural products, he points out, must hereafter be priced on the basis of the value of their chemical components. Thus cotton will come to be valued on its alpha-cellulose content, competing in this with low-cost alpha-cellulose from wood. Corn cannot expect to be valued above the sum of the values of its components. Conceiving agriculture to be at the "chemo-genetic stage," the author foresees failure unless farm management and such undertakings as the Federal Farm Board lean heavily upon what the chemists, physicists, and biologists can tell them. The term "bonaire" is suggested for air-conditioning, and it is predicted that the bonaire-motive industry is likely to surpass the automotive industry. Here, as elsewhere the author coins new words the better to express his thoughts. In a series of chapters on the relation of chemistry to four important activities—mining, agriculture, manufacture, and transportation—many interesting predictions are made as to the trend of developments when once science is fully utilized. Some novel economic thoughts are put forward in the chapter on "chemeconomics." In the chapter on Human History in Chemical Perspective the various ages are noted; following the Steel age, 1856 to 1932, the "Magal" age is placed, referring to light metal alloys of magnesium and of aluminum. The "Neoplastic" age is given the interval from 1910 to 1950 and is to be succeeded by a "Silicoplastic" age, in which the author predicts a new type of plastic of extraordinary characteristics. The "Metalloplastic" age may be expected toward the close of this century.

The triumph of chemistry is to come when nature and man effect that which only nature heretofore controlled, and the author foresees the time when whatever the race requires will be produced without fear of exhausting natural resources, through chemical application in a degree as yet little imagined. Many readers may not agree with the author's points of view but they are sure to find the work stimulating of thought and conducive to argument.

NATURAL VARNISH RESINS. *By T. Hedley Barry.* 294 pages. Ernest Benn, Ltd., 8 Bouverie St., E. C. 4, London, 1932. Price 42 s.

This book is based upon the section on Natural Resins which the author contributed to "Natural and Synthetic Resins" by T. Hedley Barry, R. S. Morrell, and Alan A. Drummond, published in 1926. It is, however, a much more complete and comprehensive treatment of the subject, the only part not rewritten being a general discussion of the botanical origin of resins, covering only 3 pages.

The history, general origin, and general physical and chemical properties of natural resins are given in the first 43 pages. The rest of the book deals with specific groups of resins or individual resins, and is the most up-to-date and well-presented description of these materials that the reviewer has seen. The numerous references given in the text, many of which are to publications that appeared in 1931, are convincing evidence of the author's grasp of the literature on resins. The numerous illustrations are well selected and executed; the maps showing geographic origin are helpful to the reader; and the statistical tables are informative. The name, botanical, and subject indices are excellent.

The omission of any statement that Red Accroides (page 123) is frequently known as Yacca gum is unfortunate from the standpoint of American readers. The statement (page 146) that Burgundy pitch is obtained from the oleoresin of *Pinus maritima* is not in accord with the common idea that it is obtained from the Norway spruce (*Picea abies*).

The British specifications for shellac varnish and unbleached unadulterated shellac (page 273) are, in the reviewer's opinion, better than the present American specifications.

Percy H. Walker

DIE CHEMISCHE UNTERSUCHUNG VON WASSER UND ABWASSER. *By J. Tillmans.* 2nd edition. 252 pages, 28 figures. Wilhelm Knapp, Halle (Saale), 1932. Price, bound, 19 marks.

This book contains 152 pages on water and 82 pages on sewage. An especially valuable feature is the inclusion of detailed discussion of the significance of analytical results, the interpretation of various tests, and the use of selected tests for investigations of water supplies, boiler water, and sewage treatment plants. The sections on "aggressive" waters, boiler waters, and water softening are valuable. The effects of oxygen and carbon dioxide on corrosion are discussed at length, with useful information from the author's long and unique experience in this field. The section on sewage analysis is noteworthy for the discussion of many chemical determinations not ordinarily encountered, but this part of the work might also be criticized as not being sufficiently selective or up to date. For example, the carbon determination as given by König in 1901 could be omitted as a needlessly cumbersome procedure, since more practical methods have since been developed. Much more material of 20 and 30 years ago could well have been elided.

Whatever fault this book has may be laid primarily to its being too inclusive. This very fact, however, explains why the work is unique, and, in the reviewer's opinion, superior to any volume now available in English on the same subject. There is a real need for such a book in English. Tillmans' treatise is devoted almost exclusively to German technic and practice.

F. W. Mohlman

DIE KÜNSTLICHEN KOHLEN FÜR ELEKTRISCHE OFEN, ELEKTROLYSE UND ELEKTROTECHNIK. *By Kurt Arndt.* 336 pages. Julius Springer, Berlin, 1932. Price, bound, 38 marks.

Kurt Arndt has rewritten the book by J. Zellner on the same subject and has added a great deal of subject matter, technical data, and illustrations which have resulted from his own research work in this field.

A complete review is given of the raw materials used in the manufacture of industrial carbon. It is copiously illustrated with microphotographs showing the characteristic physical structures of the various materials. Many illustrative analyses are given covering the essential chemical constituents and physical properties. Methods of preparing the raw materials for use are described, such as drying and both low- and high-temperature calcination. Illustrations are given of many of the various types of apparatus available for carrying out these operations. Preparation of the plastic carbon paste and formation of this paste into the desired shape is described. Illustrations are given of apparatus available for carrying out the various steps in this preparation, such as crushing, grinding, and sizing of the grain, mixing of the grain and bond, and forming of the paste in the desired shape. The baking of the carbon shape to set the bond and the furnaces used for carrying out this operation are described. Methods of graphitization are discussed, and a comparison is given of the essential properties of graphitized product from various raw materials as compared with the similar materials baked to a lower temperature.

The author makes clear not only the procedures and apparatus used in the preparation of industrial carbon in general but describes and illustrates any special procedures which are required in the preparation of electrodes for both electrothermal and electrolytic processes, lighting carbons, brushes, and specialties such as battery elements, microphone carbon, and resistors. Methods of determining the essential physical and electrical characteristics of these various classes of industrial carbon are given, and apparatus for carrying out these determinations is illustrated.

In the case of the electrothermal processes using industrial carbon—for example, the preparation of calcium carbide, ferro alloys, and electric steel—a description is given not only of the use of the big carbon electrodes but also of the Soderberg self-baking electrodes. Many other processes using industrial carbon are described, such as the manufacture of silicon carbide and fused alumina abrasives; the fused electrolyte industries (such as the preparation of aluminum), and the aqueous electrolyte industries (such as the chlorine caustic soda cell) are discussed and illustrated.

While the book in some places has rather the appearance of an apparatus catalog, it is nevertheless a comprehensive summary of the preparation and uses of industrial carbon.

A. T. Hinckley

DIE KÄLTEMASCHINE. GRUNDLAGEN, AUSFÜHRUNG, BETRIEB, UNTERSUCHUNG UND BERECHNUNG VON KÄLTEANLAGEN. *By M. Hirsch.* 2nd edition. 657 pages, 390 illustrations and diagrams. Julius Springer, Berlin, 1932. Price, 36 marks.

This treatise is an elaborate presentation of the whole subject of the machinery of mechanical refrigeration and air-conditioning, as well as the methods and technic of operation. It is the second edition, amplified and thoroughly revised, bringing the subject up to date.

The contents are arranged systematically under four general heads: fundamental principles, operation of the various types of refrigeration machines, management and tests, mathematical computations.

In addition to the complete table of contents, there are three separate indices: authors, inventors, and pioneers in the field of refrigeration; general index; list of manufacturing firms and corporations. All these are international in scope and facilitate the use of the book as a work of reference.

Not the least useful feature is a list of formulas, signs, and abbreviations which will prove especially helpful to those not too familiar with technical German. Distributed throughout are 390 diagrams and illustrations, the latter covering refrigeration machinery and methods used in different countries, not a few being of American origin.

The book is clearly and handsomely printed on an excellent grade of paper and is serviceably bound in durable black cloth. As a further contribution to the large and growing literature of mechanical refrigeration it should be useful, both as a works handbook and more especially as a text in the engineering departments of technical schools and universities.

C. H. Ehrenfeld

CHEMISCHE TECHNOLOGIE DER LÖSUNGSMITTEL. *By Otto Jordan.* 322 pages. Julius Springer, Berlin, 1932. Price, 26.50 marks.

This is an excellent book. It covers the field of organic solvents and softeners, the use of which has expanded so enormously during the past 10 years. The subject matter is well arranged and remarkably up to date. After a brief general introduction the author discusses the physical characteristics of solvents in general; solvents for cellulose derivatives; solvents for resins, rubber, and other plastics; solvents for extraction purposes; softeners and their action on cellulose derivatives, rubber, resin, and other plastics; the physiological action of solvents; solvent recovery; safety measures to be followed in the production and use of solvents; methods for analyzing products containing solvents; the manufacture of solvents in general; and finally a discussion of each individual solvent and softener in particular with its physical characteristics and the author's opinion as to its utility.

The book differs from many works of this nature in that it is not simply a compilation from the literature with much contradictory material. It is a reflection of the opinions of the author who evidently knows his subject thoroughly. For example, on page 159 he gives two methods for the analytical separation of aliphatic and aromatic hydrocarbons and then says: "Numerous other methods for the separation of benzine are less simple." The analytical methods given are the best that the reviewer has seen published to date.

In any book of this nature, there are bound to be a few opinions expressed with which other workers in the field will not agree. For example (page 71), he condemns the American methods of measuring viscosities by the falling ball method, especially in measuring "$^1/_2$ second" and "$^1/_4$ second" nitrocelluloses. He evidently does not realize that these expressions are merely empirical trade terms—as a matter of fact, it requires $^1/_4$ of a second for a ball to fall one foot in a vacuum. There are remarkably few cases, however, in which his views will be found at variance with those of other workers.

The material is presented in a clear, simple manner, and even those who do not read German fluently will find the book easy to use.

Guy C. Given

ÜBER DEN ZERFALL DER BITUMINÖSEN STRASSENBAU-EMULSIONEN DURCH BERÜHRUNG MIT DEM GESTEIN. *By Hans Weber and Hermann Bechler.* 9 pages. Allgemeiner Industrie Verlag G. m. b. H., Stresemannstrasse 27, Berlin SW 11, 1932. Price, 4.50 marks.

The rise in importance of bituminous emulsions for use in road work is described. The rapid increase in their use is attributed to ease of application and low cost. A study of the failures of certain jobs makes clear the fact that, for different work, emulsions of different properties must be used. What tests shall be used to determine the requisite properties that a bituminous emulsion must possess to meet specific construction and service requirements? The answer to this question is the prupose of the publication.

The breaking of emulsions is of utmost importance to the practical road builder. This property is the basis of the method developed by the authors. In general, their method consists of mixing a weighed amount of stone of definite grain size with the emulsion. The two are permitted to react without evaporation of water. The part of the emulsion not reacted upon is washed out with water. The remaining bitumen-stone mass is weighed after drying. The method described is useful in that it places on a quantitative basis a property which has been heretofore used only in a qualitative way. It has been developed with great thoroughness. Different individuals can check themselves more easily than they can check each other. The authors ascribe this difference to the manner of washing the bitumen-stone mix, and they plan to define this step more specifically. The reviewer was impressed with the thoroughness with which the method was investigated to determine its reliability. It was used for determining the stability of various emulsion preparations and the reactivity of various petrographic materials used in road building.

The authors base their explanation of the "breaking" process on adsorption of the alkali contained in the emulsion by the stone at its surface. Adsorption describes the action rather vaguely. Whether it promotes a compound formation due to primary valence forces or is merely a concentration due to other causes, is not established. The development of a trustworthy and simple method such as is described in this paper for determining the "breaking value" of bituminous emulsion is a timely contribution to the bituminous emulsion technology. It has apparently given to the industry a reliable new tool. It is recommended to the American Society for Testing Materials for consideration.

A few inconsistencies are noted. On page 33, Table 16, No. II, maximum difference between individual observers is given as 4, when from Table 14, page 32, it appears to be 3.8. In sections II and V, subdivisions are marked by numbers, in section III by letters.

A. W. Hixson

* * *

Annali. Vol. II. Laboratorio di ricerche sulle fermentazioni Lazzaro Spallanzani. 558 pages. R. Instituto Superiore Agrario di Milano, and Laboratorio di Chimica Agraria, E. Stazione Agraria Sperimentale, Milan, 1932. Price, 40 lire.

A. S. T. M. Tentative Standards. 1236 pages. American Society for Testing Materials, 1315 Spruce St., Philadelphia, 1932. Price, paper, $7.00; cloth, $8.00.

MARKET REPORT—DECEMBER, 1932

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, DECEMBER 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

Newer Chemicals

Acetaldehyde, drums, lc-l., wks	lb.	.18½
Acetaldol, 50-gal. drums	lb.	.27
Acetylene tetrachloride, *see* Tetrachloroethane		
Acid, abietic	lb.	.12
Adipic	lb.	.72
Furoic, tech., drums	lb.	.35
Linoleic	lb.	.16
Sebacic, tech	lb.	.58
Ammonium linoleate, drums	lb.	.11
Ammonium oleate	lb.	.10
Amyl furoate, 1-lb. tins	lb.	5.00
Aroclors	lb.	.40
Butyl carbitol, *see* Diethylene glycol monobutyl ether		
Cellosolve, *see* Ethylene glycol monobutyl ether		
Furoate, tech., 50-gal. drums	lb.	1.00
Calcium furoate, tech., drums	lb.	.30
Capryl alcohol, tech	lb.	.85
Pure	lb.	2.50
Carbitol, *see* Diethylene glycol monoethyl ether		
Cellosolve, *see* Ethylene glycol monoethyl ether		
Acetate, *see* Ethylene glycol monoethyl ether acetate		
Crotonaldehyde, 50-gal. drums	lb.	.32
Dichloroethyl ether, 50-gal. drums	lb.	.16
Diethylene glycol, drums	lb.	.14
Monobutyl ether, drums	lb.	.26
Monoethyl ether, drums	lb.	.15
Diethylene oxide, 50-gal. drums	lb.	.26
Dioxan, *see* Diethylene oxide		
Diphenyl	lb.	.20
Ethyl acetoacetate, 110-gal. drums	lb.	.37
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.	.0595
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.	.45
Glyceryl phthallate	lb.	.26
Glycol stearate	lb.	.18
Isopropyl ether, drums	lb.	.10
Lead dithiofuroate, 100-lb. drums	lb.	1.00
Magnesium peroxide, 100-lb. cs	lb.	1.15
Methyl acetate, 82%, drums	lb.	.12
99%	lb.	.15
Cellosolve, *see* Ethylene glycol monomethyl ether		
Furoate, tech., 50-gal. drums	lb.	.50
Methyl hexyl ketone, pure	lb.	1.20
Paraldehyde, 110–55 gal. drums	lb.	.20½
Phosphorus oxychloride, 175 cyl	lb.	.20
Potassium abietate	lb.	.06
Propyl furoate, 1-lb. tins	lb.	2.50
Sodium abietate	lb.	.03
Sodium alginate	lb.	.50
Strontium peroxide, 100-lb. drums	lb.	1.25
Sulfuryl chloride, 600-lb. drums, crude	lb.	.15
Distilled	lb.	.40
Tetrachloroethane, 50-gal. drums	lb.	.08
Trichloroethylene, 50-gal. drums	lb.	.10
Triethanolamine, 50-gal. drums	lb.	.35
Trihydroxyethylamine linoleate	lb.	.40
Trihydroxyethylamine stearate	lb.	.35
Vinyl chloride, 16-lb. cyl	lb.	1.00
Zinc dithiofuroate, 100-lb. drums	lb.	1.00
Perborate, 100-lb. drums	lb.	1.25
Peroxide, 100-lb. drums	lb.	1.25

Chemicals Previously Quoted

Acetanilide, U. S. P., powd., bbls	lb.	.26
Acetic anhydride, 92–95%, cbys	lb.	.21
Acetone, drums, wks	lb.	.10¼
Acetphenetidin, bbls	lb.	1.25
Acid, acetic, 28%, c/l., bbls	100 lbs.	2.75
56%, c/l., bbls	100 lbs.	5.10
Glacial, c/l., bbls	100 lbs.	9.14
Glacial, U. S. P., c/l., carboys	100 lbs.	9.64
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.	.11¾
Cinnamic, bottles	lb.	3.25
Citric, U. S. P., cryst., bbls	lb.	.29
Cresylic, pale, drums	gal.	.42
Formic, 90%, cbys., N. Y	lb.	.10¼
Gallic, U. S. P., bbls	lb.	.74
Glycerophosphoric, 25%, 1-lb. bot	lb.	1.40
H, bbls., wks	lb.	.65
Hydriodic, 10%, U. S. P., 5-lb. bot	lb.	.67
Hydrobromic, 48%, cbys., wks	lb.	.45
Hydrochloric, 20°, tanks, wks	100 lbs.	1.35
Hydrofluoric, 30%, bbls., wks	lb.	.06
60%, bbls., wks	lb.	.13
Hydrofluosilic, 35%, bbls., wks	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis	lb.	.75
Lactic, 22%, dark, bbls	lb.	.04
48%, light, bbls., wks	lb.	.11
Mixed, tanks, wks	N unit	.07
	S unit	.08
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls	lb.	nom.
Nitric, C. P., cbys	lb.	.11
Nitric, 36°, c/l., cbys., wks	100 lbs.	5.00
Oxalic, bbls., wks	lb.	.11
Phosphoric, 50%, U. S. P	lb.	.14
Picramic, bbls	lb.	.65
Picric, bbls., c/l	lb.	.30
Pyrogallic	lb.	1.45
Salicylic, tech., bbls	lb.	.33
Stearic. d. p., bbls., c/l	lb.	.07½
Sulfanilic, 250-lb. bbls	lb.	.14½
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.	.20
Tungstic, kegs	lb.	1.40
Valeric, C. P., 10-lb. bot	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls	gal.	2.56½
Amyl, from pentane, tanks	lb.	.176
Amyl, Imp. drums	gal.	1.75
Butyl, drums, c/l., wks	lb.	.123
Cologne spirit, bbls	gal.	2.69
Denatured, No. 5, comp. denat., c/l., drums	gal.	.396*
Isoamyl, drums	gal.	4.00
Isobutyl, ref., drums	gal.	.75
Isopropyl, ref., drums	gal.	.45
Propyl, ref., drums	gal.	.75
Wood, *see* Methanol		
Alpha-naphthol, bbls	lb.	.57
Alpha-naphthylamine, bbls	lb.	.32

---

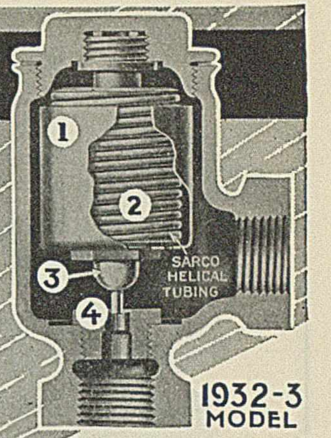
*Delivered metropolitan area.

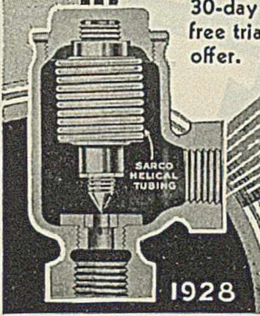
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.30
Chrome, casks, wks	100 lbs.	4.50
Potash, lump, bbls., wks	100 lbs.	3.35
Soda, bbls., wks	100 lbs.	3.45
Aluminum, metal, N. Y	100 lbs.	22.90
Aluminum chloride, anhyd., commercial, wks., drums extra, c/l	lb.	.05
Aluminum stearate, 100-lb. bbl	lb.	.15
Aluminum sulfate, comm'l, bags, wks	100 lbs.	1.25
Iron-free, bags, wks	100 lbs.	1.90
Aminoazobenzene, 100-lb. kegs	lb.	1.15
Ammonia, anhydrous, cyl., wks	lb.	.15½
50,000-lb. tanks, wks	lb.	.05
Ammonia, aqua, 26°, tanks, wks., contained NH_3	lb.	.05½
Ammonium acetate, kegs	lb.	.33
Bifluoride, bbls	lb.	.21
Bromide, 50-lb. boxes	lb.	.35
Carbonate, tech., casks	lb.	.08
Chloride, gray, bbls	100 lbs.	5.25
Lump, casks	lb.	.10½
Iodide, 25-lb. jars	lb.	5.20
Nitrate, tech., cryst., bbls	lb.	.08½
Oxalate, kegs	lb.	.22
Persulfate, cases	lb.	.20
Phosphate, dibasic, tech., bbls	lb.	.08½
Sulfate, bulk, wks	ton	20.50
Amyl acetate, tech., from pentane, tanks	lb.	.157
Aniline oil, drums	lb.	.14½
Anthracene, 80–85%, casks, wks	lb.	.60
Anthraquinone, subl., bbls	lb.	.45
Antimony, metal	lb.	.05⅞
Antimony chloride, drums	lb.	.13
Oxide, bbls	lb.	.07½
Salt, dom., bbls	lb.	.20
Sulfide, crimson, bbls	lb.	.25
Golden, bbls	lb.	.16
Vermilion, bbls	lb.	.38
Argols, red powder, bbls	lb.	.07
Arsenic, metal, kegs	lb.	.27
Red, kegs, cases	lb.	.09⅜
White, c/l., kegs	lb.	.04
Asbestine, bulk, c/l	ton	15.00
Barium carbonate, bbls., bags, wks	ton	47.00
Chloride, bbls., wks	lb.	.03¾
Dioxide, drs., wks	lb.	.12
Hydroxide, bbls	lb.	.05¼
Nitrate, casks	lb.	.07
Barium thiocyanate, 400-lb. bbls	lb.	.27
Barytes, floated, 350-lb. bbls., wks.	ton	23.00
Benzaldehyde, tech., drums	lb.	.60
F. F. C., cbys	lb.	1.40
U. S. P., cbys	lb.	1.15
Benzidine base, bbls	lb.	.65
Benzol, tanks, wks	gal.	.20
Benzoyl chloride, drums	lb.	.40
Benzyl acetate, F. F. C., bottles	lb.	.75
Alcohol, drums	gal.	.75
Chloride, tech., drums	lb.	.30
Beta-naphthol, bbls	lb.	.22
Beta-naphthylamine, bbls	lb.	.58
Bismuth, metal, cases	lb.	.90
Bismuth, nitrate, 25-lb. jars	lb.	.95
Oxychloride, boxes	lb.	2.95
Subnitrate, U. S. P., 25-lb. jars	lb.	1.10
Blanc fixe, dry, bbls	ton	65.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls	lb.	.08¼
Borax, bags	lb.	.018
Bordeaux mixture, bbls	lb.	.11½
Bromine, bot	lb.	.36
Bromobenzene, drums	lb.	.50
Bromoform, jars	lb.	1.80
Butyl acetate, drums, c/l	lb.	.159
Cadmium bromide, 50-lb. jars	lb.	1.40
Cadmium, metal, cases	lb.	.55

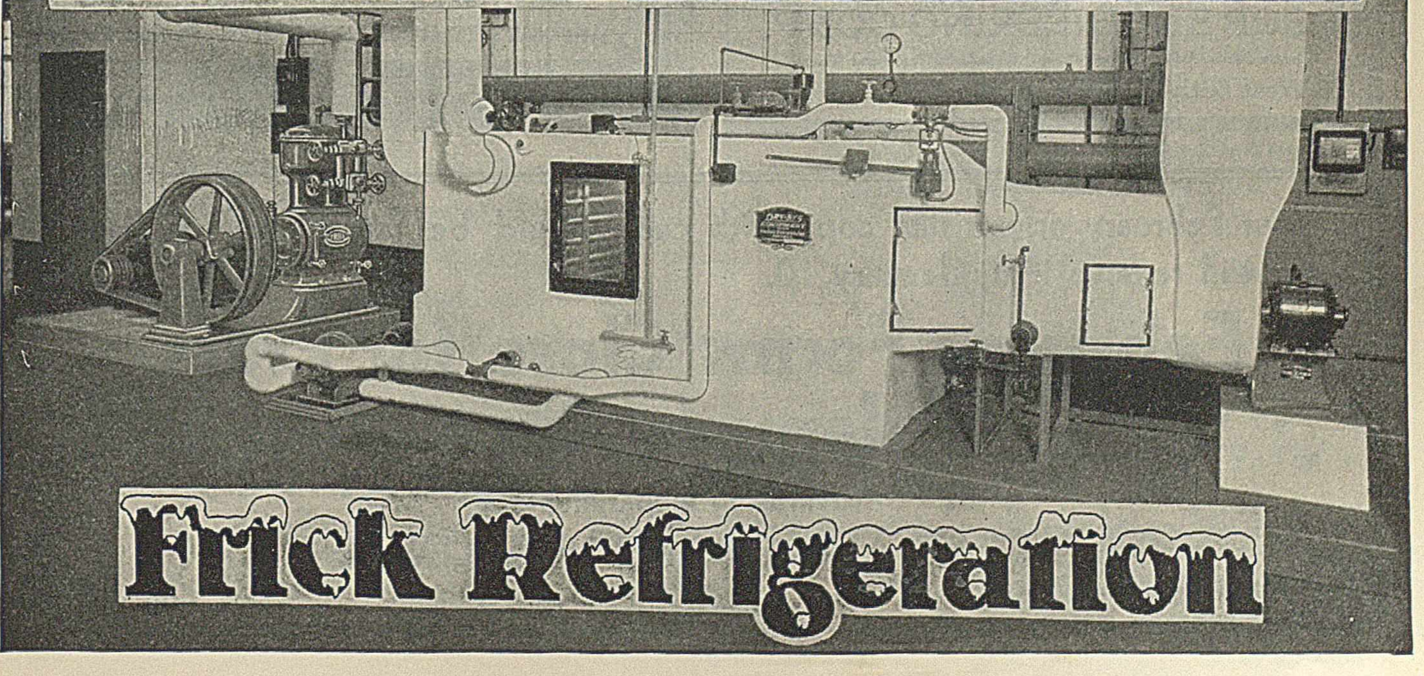
Cadmium sulfide, boxes	lb.	.60
Caffeine, U. S. P., 5-lb. cans	lb.	2.40
Calcium acetate, bags	100 lbs.	2.50
Arsenate, bbls.	lb.	.05½
Carbide, drums	lb.	.05½
Chloride, drums, wks., flake	ton	21.00
Cyanide, 100-lb. drums	lb.	.30
Nitrate, bags	ton	35.00
Phosphate, monobas., bbls.	lb.	.07½
Tribas., bbls.	lb.	.11
Calcium carbonate, tech., bags,	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl.	lb.	.06½
Camphor, Jap., slabs	lb.	.36½
Carbazole, bbls.	lb.	.75
Carbon, activated, drums	lb.	.08
Carbon bisulfide, drums	lb.	.051
Carbon black	lb.	.0275
Carbon dioxide, liq. cyl.	lb.	.06
Carbon tetrachloride, drums	lb.	.06¼
Casein, stand. gr., bbls.	lb.	.06½
Cellulose acetate, bbls.	lb.	.80
Cerium oxalate, kegs	lb.	.33
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.	1.55
Chlorobenzene, mono-, drums	lb.	.06
Chloroform, tech., drums	lb.	.15
Chromium acetate, 20° soln., bbls.	lb.	.05
Coal tar, bbls., wks.	gal.	.10
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls.	lb.	1.25
Cod-liver oil, bbls.	bbl.	30.00
Copperas, c/l., bulk	ton	14.50
Copper, metal, elec.	100 lbs.	5.36
Copper carbonate, bbls., 52/54%	lb.	.15½
Chloride, bbls.	lb.	.22
Cyanide, drums	lb.	.39
Oxide, red, bbls.	lb.	.15¼
Sulfate, c/l., bbls.	100 lbs.	3.00
Cotton, soluble, bbls.	lb.	.40
Cream tartar, bbls.	lb.	.15½
Cyanamide, bulk, N. Y.	Ammonia unit	.97½
Diaminophenol, kegs	lb.	3.80
Dianisidine, bbls.	lb.	2.35
Dibutylphthalate, drums, wks.	lb.	.218
Diethylaniline, drums	lb.	.55
Diethylene glycol, drums	lb.	.14
Diethyl phthalate, drums	lb.	.23
Diethyl sulfate, tech., drums	lb.	.20
Dimethylaniline, drums	lb.	.26
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.15½
Dinitrochlorobenzene, bbls.	lb.	.13
Dinitronaphthalene, bbls.	lb.	.34
Dinitrophenol, bbls.	lb.	.23
Diphenylamine, bbls.	lb.	.34
Diphenylguanidine, bbls.	lb.	.30
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.70
Ether, nitrous, bot.	lb.	.80
Ether, conc., drums	lb.	.09
Ethyl acetate, tanks, c/l.	lb.	.09
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.	.25
Feldspar, bulk	ton	6.50
Ferric chloride, tech., bbls.	lb.	.04½
Ferrous chloride, cryst., bbls.	lb.	.06
Ferrous sulfide, bbls.	100 lbs.	2.50
Fluorspar, 98%, bags	ton	31.00
Formaldehyde, bbls.	lb.	.06
Formaniline, drums	lb.	.37½
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural, drums, tech., contract, works	lb.	.10
Glauber's salt, bbls.	100 lbs.	1.00
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerine, C. P., drums	lb.	.09¾
G salt, bbls.	lb.	.42
Hexamethylenetetramine, tech., drums	lb.	.46
Hydrogen peroxide, 25 vol., bbls.	lb.	.05½
Hydroquinone, kegs	lb.	1.20
Indigo, 20%, paste, bbls.	lb.	.12
Iodine, crude, 200-lb. kgs.	lb.	4.20
Iodine, resubl., jars	lb.	4.65
Iodoform, bot.	lb.	6.00
Iridium, metal	oz.	160.00
Kieselguhr, bags	ton	50.00
Lead, metal, N. Y.	100 lbs.	3.00
Lead acetate, bbls., white	lb.	.10½
Arsenate, bbls.	lb.	.08½
Oxide, litharge, bbls.	lb.	.05¾
Peroxide, drums	lb.	.20
Red, bbls.	lb.	.06¾
Sulfate, bbls.	lb.	.06¼
White, basic carb., bbls.	lb.	.07¼
Lime, hydrated, bbls.	100 lbs.	.85
Lime, live, chemical, bbls., wks.	100 lbs.	1.05
Limestone, ground, bags, wks.	ton	4.50
Lithopone, bbls.	lb.	.04½
Magnesite, crude	ton	32.00
Calcined, 500-lb. bbls., wks.	ton	40.00
Magnesium, metal, wks.	lb.	.30
Magnesium carbonate, bags	lb.	.05¼
Chloride, drums	ton	36.00
Fluosilicate, cryst., bbls.	lb.	.10
Oxide, U. S. P., light, bbls.	lb.	.42
Manganese chloride, casks	lb.	.07½
Dioxide, 80%, bbls.	ton	80.00
Sulfate, casks	lb.	.07
Mercury bichloride, cryst., 50 lbs.	lb.	1.31
Mercury, flasks, 76 lbs.	flask	49.00
Meta-nitroaniline, bbls.	lb.	.67
Meta-phenylenediamine, bbls.	lb.	.80
Meta-tolylenediamine, bbls.	lb.	.67
Methanol, pure, synthetic, drums, delivered	gal.	.37½
Tanks, delivered	gal.	.35½
Methyl acetone, drums	gal.	.47
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.45
Michler's ketone, bbls.	lb.	3.00
Naphtha, solvent, tanks	gal.	.26
Naphthalene, flake, bbls.	lb.	.04¾
Nickel, metal	lb.	.35
Nickel salt, single, bbls.	lb.	.11
Double, bbls.	lb.	.11
Niter cake, bulk	ton	11.50
Nitrobenzene, drums	lb.	.08½
Oil, castor, No. 1	lb.	.09½
China wood, bbls.	lb.	.05½
Coconut, Ceylon, tanks	lb.	.03½
Cod, N. F., bbls.	gal.	.23
Corn, crude, tanks, mills	lb.	.02⅞
Cottonseed, crude, tanks	lb.	.03⅝
Lard, edible, bbls.	lb.	.08½
Linseed, bbls.	lb.	.068
Menhaden, crude, tanks	gal.	.09½
Neat's-foot, pure, bbls.	lb.	.08
Oleo, No. 1, bbls.	lb.	.06
Olive oil, denat., bbls.	gal.	.58
Foots, bbls.	lb.	.04⅜
Palm, Lagos, casks	lb.	.04
Peanut, crude, tanks	lb.	.03¼
Perilla, bbls.	lb.	.04½
Rapeseed, bbls., English	gal.	.31
Red, bbls.	lb.	.06½
Soy bean, crude, tanks	lb.	.0275
Sperm, 38°, bbls.	gal.	.68
Whale, bbls., natural, winter	gal.	.56
Ortho-aminophenol, kegs	lb.	2.15
Ortho-dichlorobenzene, drums	lb.	.08
Ortho-nitrochlorobenzene, drums	lb.	.28
Ortho-nitrophenol, bbls.	lb.	.85
Ortho-nitrotoluene, drums	lb.	.16
Ortho-toluidine, bbls.	lb.	.20
Palladium, metal	oz.	19.00
Para-aminophenol, kegs	lb.	.78
Para-dichlorobenzene	lb.	.15½
Para-formaldehyde, cases	lb.	.38
Paraldehyde, tech., drums	lb.	.20½
Para-nitraniline, drums	lb.	.48
Para-nitrochlorobenzene, drums	lb.	.25
Para-nitrophenol, bbls.	lb.	.45
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls.	lb.	.29
Para-phenylenediamine, bbls.	lb.	1.15
Para-toluidine, bbls.	lb.	.40
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.	.42
Phosphorus trichloride, cyl.	lb.	.18
Phthalic anhydride, bbls.	lb.	.15
Platinum, metal	oz.	37.50
Potash, caustic, drums	lb.	.06⅛
Potassium acetate, kegs	lb.	.28
Bicarbonate, casks	lb.	.09½
Bichromate, casks	lb.	.07
Binoxalate, bbls.	lb.	.14
Bromide	lb.	.32
Carbonate, 80–85%, calc., casks	lb.	.05
Chlorate, kegs	lb.	.08
Chloride, crystals, bbls.	lb.	.04¾
Cyanide, cases	lb.	.50
Meta-bisulfite, bbls.	lb.	.10½
Muriate, fert., bulk	ton	35.55
Permanganate, drums	lb.	.16
Prussiate, red, casks	lb.	.37½
Yellow, casks	lb.	.16½
Titanium oxalate, bbls.	lb.	.21
Pyridine, drums	gal.	.85
Resorcinol, tech., kegs	lb.	.65
Rochelle salt, bbls., U. S. P.	lb.	.12½
R salt, bbls.	lb.	.42
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.	.20
Soda ash, 58%, light, bags, contract, wks.	100 lbs.	1.20
Soda, caustic, 76%, solid, drums, contract, wks.	100 lbs.	2.55
Sodium acetate, bbls.	lb.	.05
Benzoate, bbls.	lb.	.42
Bicarbonate, bbls.	100 lbs.	1.85
Bichromate, casks	lb.	.04½
Bisulfite, bbls.	lb.	.04
Bromide, bbls., U. S. P.	lb.	.31
Chlorate, kegs	lb.	.05¾
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.15½
Fluoride, bbls.	lb.	.07
Metallic, drums, 12¼-lb. bricks	lb.	.19
Metasilicate, cryst.	100 lbs.	3.25
Metasilicate, gran., bbls.	100 lbs.	2.85
Naphthionate, bbls.	lb.	.52
Nitrate, crude, 200-lb. bags, N. Y.	100 lbs.	1.26
Nitrite, bbls.	lb.	.07
Perborate, bbls.	lb.	.17
Peroxide, cases	lb.	.21
Phosphate, trisodium, bbls.	100 lbs.	2.15
Phosphate, disodium, bags	100 lbs.	1.80
Picramate, kegs	lb.	.69
Prussiate, bbls.	lb.	.11½
Silicate, drums, tanks, 40°	100 lbs.	.75
Silicofluoride, bbls.	lb.	.05¾
Stannate, drums	lb.	.18
Sulfate, anhyd., bbls.	lb.	.02
Sulfide, cryst., bbls.	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls.	lb.	.28
Thiosulfate, reg., cryst., bbls.	lb.	.02½
Tungstate, kegs	lb.	.60
Strontium carbonate, tech., bbls.	lb.	.07¼
Nitrate, bbls.	lb.	.09
Sulfur, bulk, mines, wks.	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
Sulfur dioxide, commercial, cyl.	lb.	.07
Sulfuryl chloride, drums	lb.	.10
Thiocarbanilid, bbls.	lb.	.26½
Tin	lb.	.23⅜
Tin tetrachloride, anhydrous, drums, bbls.	lb.	.1440
Oxide, bbls.	lb.	.24½
Titanium dioxide, bbls., wks.	lb.	.17¼
Toluene, tanks	gal.	.30
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.58
Triphenyl phosphate, bbls.	lb.	.60
Tungsten, powder	lb.	1.65
Urea, pure, cases	lb.	.11
Whiting, bags	100 lbs.	1.00
Xylene, 10°, tanks, wks.	gal.	.26
Xylidine, drums	lb.	.36
Zinc, metal, E. St. Louis	100 lbs.	3.15
Zinc ammonium chloride, bbls.	lb.	.05
Chloride, granulated, drums	lb.	.05⅜
Oxide, Amer., bbls.	lb.	.05¼
Stearate, bbls.	lb.	.16
Zinc dust, bbls., c/l.	lb.	.041

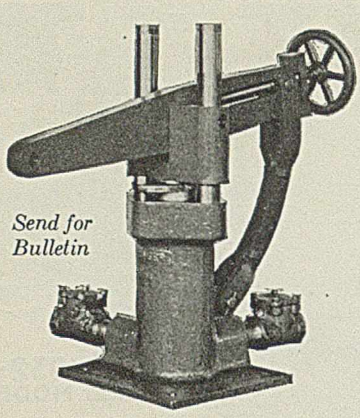
---

* F. O. B. destination.


1
2
3
4
SARCO HELICAL TUBING
1932-3 MODEL


SARCO HELICAL TUBING
1928




Send for Bulletin

PIONEER ALLOYS

Strength Ductility

For Practically All Acid, Heat and Erosion Conditions

Castings and Cast Pipe Valves and Fittings

Proportioning Pumps

Not one Alloy—but the Right one for Your Needs

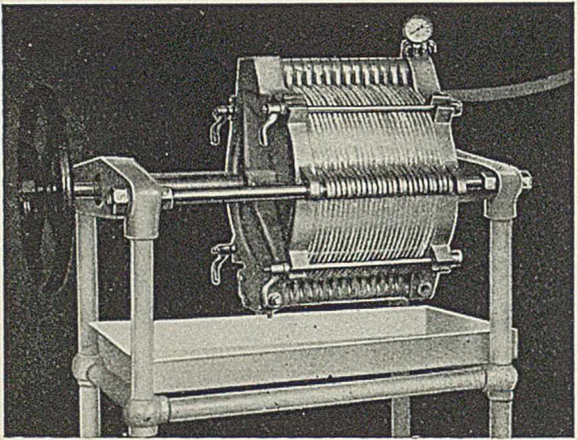
We have served the Process Industries for 12 Years

PIONEER ALLOY PRODUCTS CO., INC.

16603 Euclid Avenue Cleveland, Ohio

FILTRATION . . . . 1st Stage

CLARIFICATION 2nd Stage



HOW MUCH can still be taken out of your filtered liquid you will never know until we have shown you by a free clarification test, without any obligation on your part.

KEEP your filter presses. You will need them more when we show you how to improve their product.

Follow this up. Ask us for details. We will instruct you how to submit a sample for our free test.

ALSOP ENGINEERING CORP.

Electric Filters, Asbestos Discs, Pumps, Glass Lined Tanks and Mixers

39 West 60th Street New York, N. Y.

In the Industrial and Chemical Fields

Insist upon U S S STAINLESS Steel Sheets—produced in a number of grades and finishes, and adapted to a wide range of applications. Write for literature and full information on the following alloys—

U S S CHROMIUM-NICKEL Steels, *Austenitic:* 18-8; 18-12; 25-12.
U S S CHROMIUM-ALLOY Steels, *Ferritic:* 12; 17; 27.

USS Chromium-Nickel Alloy Steels produced under licenses of Chemical Foundation, Inc., New York; and Fried. Krupp A. G. of Germany.

This Company also manufactures high grade Black and Galvanized Sheets, Tin and Terne Plates for all known uses.

AMERICAN SHEET AND TIN PLATE COMPANY, Pittsburgh, Pa.

SUBSIDIARY OF UNITED STATES STEEL CORPORATION

Your February advertising copy with cuts should be forwarded so that we will receive it by January 10.

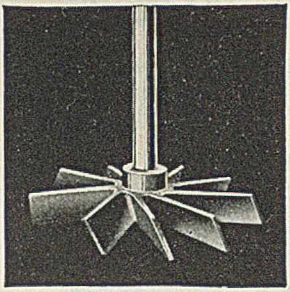
February Forms Close for Press January 15

Advertising Department

INDUSTRIAL AND ENGINEERING CHEMISTRY

419 Fourth Avenue
After January 13, 1933
330 West 42nd Street
New York

Investigate . . .



business strategy says "now"

▼

BUSINESS sense indicates that—

NOW is the time to look into new and modern equipment and its possibilities.

A thorough investigation into what modern equipment can do will mean a better product at less cost.

"New England" has much to tell you about AGITATION —about the Turbine and other types of stirrers and their applications—about types and designs of Agitator Drives.

Investigate Now!

NEW ENGLAND TANK
& TOWER COMPANY
EVERETT .... MASS.
50 CHURCH ST., ... NEW YORK

CHAS. PFIZER & CO. INC.
MANUFACTURING CHEMISTS
NEW YORK
EST 1849
REG. IN U. S. PAT. OFF.

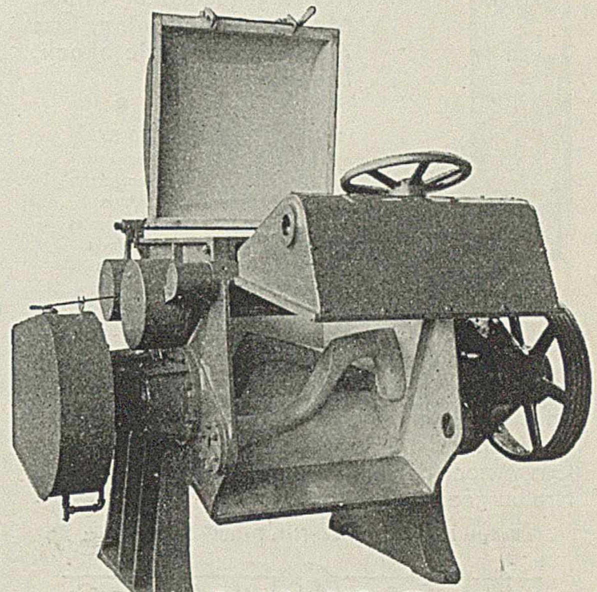
Citric Acid
Tartaric Acid
Cream Tartar
Rochelle Salt
Tartar Emetic
Bismuth Subnitrate
Bismuth Subcarbonate
Potassium Iodide
Phenolphthalein
Gluconic Acid
Iodine Resublimed
Calomel
Corrosive Sublimate
Red Precipitate
Potassium Citrate
Sodium Citrate
Strychnine & its Salts
Cinchophen
Chloroform
Calcium Gluconate

CHAS. PFIZER & CO., INC.
MANUFACTURING CHEMISTS
ESTABLISHED 1849

81 Maiden Lane
NEW YORK, N. Y.

444 West Grand Avenue
CHICAGO, ILL.

IN AGAIN
OUT AGAIN



Size 15-Type IV-Class BS with counterbalanced front discharge door and counterbalanced cover, both shown in open position.

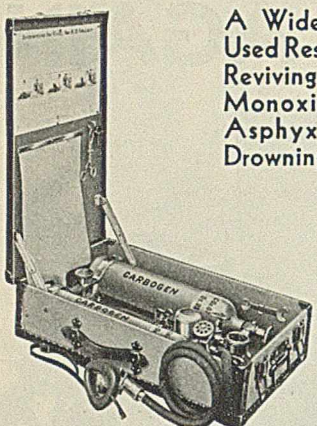
The job for which this W & P Mixer & Kneader was designed is a rapid fire job.
The blades rotate at very high speeds;
the mixing period is only 2 to 3 minutes;
no time must be lost in loading and unloading.
The batches are in again out again all day long.
Just a quarter-turn of the hand wheel in front and the whole front wall of the trough is open for discharge.
Just one flip of the latch and the cover is open to receive the next batch from over head.

Client wanted speed of operation.
We gave him speed.

Another proof that Baker Perkins mixers are fitted to the job.

WP
REG. U.S. PAT. OFF.

Baker Perkins Company, Inc.
Werner & Pfleiderer Division
Main Office and Plant: Saginaw, Michigan
Sales Offices in
New York, Buffalo, Chicago, San Francisco



H-H INHALATOR

A Widely and Successfully Used Resuscitation Device for Reviving Victims of Carbon Monoxide Poisoning, Gas Asphyxia, Electric Shock, Drowning, Etc.

●

ADOPTED BY
Fire Departments
Police Departments
Public Utilities
Mining Companies
Chemical Works
Oil Companies
Steel Plants
Hospitals
Ambulance Services
Etc.

The H-H INHALATOR is accepted by the Council on Physical Therapy of the American Medical Association and officially approved by the American Gas Association and Association of Police and Fire Surgeons.

Bulletin No. 80 Gives Complete Details—Send for Copy

Mine Safety Appliances Co.
Braddock, Thomas and Meade Sts., Pittsburgh, Pa.
"EVERYTHING for MINE and INDUSTRIAL SAFETY"

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

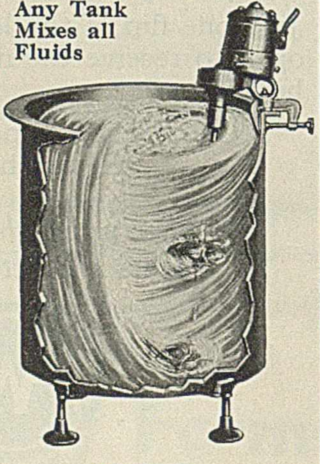
Acetate Kettle with Agitator.

GEORGE F. OTT CO.
213 Buttonwood St. Philadelphia, Pa.
Works: Phila. Cable address: "OTT" Phila.

EQUIP FOR PROFIT
WITH "LIGHTNIN" MIXERS
RESULTS GUARANTEED

- Superior Mixing With Less Machinery
- Increase Production Improve Quality
- Less First Cost Negligible Upkeep
- Utmost Simplicity Increased Efficiency
- Less Power Consumption Greater Output
- Pay for Themselves by Savings Effected

Clamp on Any Tank Mixes all Fluids



PATENTED

All Sizes—from the Laboratory to the Largest Industrial Mixing Process.

Write for Information

MIXING EQUIPMENT CO., INC.
1026 Garson Avenue, Rochester, New York
NEW YORK, N. Y. CHICAGO, ILL.

NUCLEIC ACIDS
By
P. A. LEVENE and LAWRENCE W. BASS
A. C. S. MONOGRAPH No. 56

THE CHEMIST since the earliest days of organic chemistry, has always found uric acid and its derivatives a fruitful field for research. The story of the growth of knowledge concerning the structure of these compounds, which is contained in this monograph, is closely associated with the history of theoretical organic chemistry.

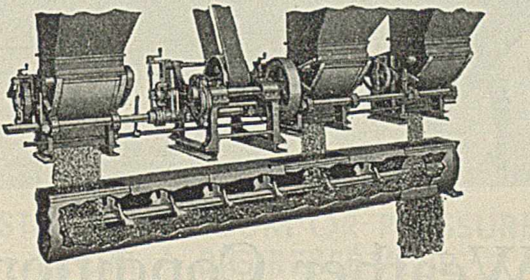
THE BIOLOGIST acquired an interest in the chemistry of nucleic acids when he realized the limitations of the microscope for the study of cells. The history of our knowledge of nucleic acids reflects the origin and development of cell chemistry with its bearing on the problems of reproduction and regeneration. This volume contains the findings of the older as well as the most recent work in this field.

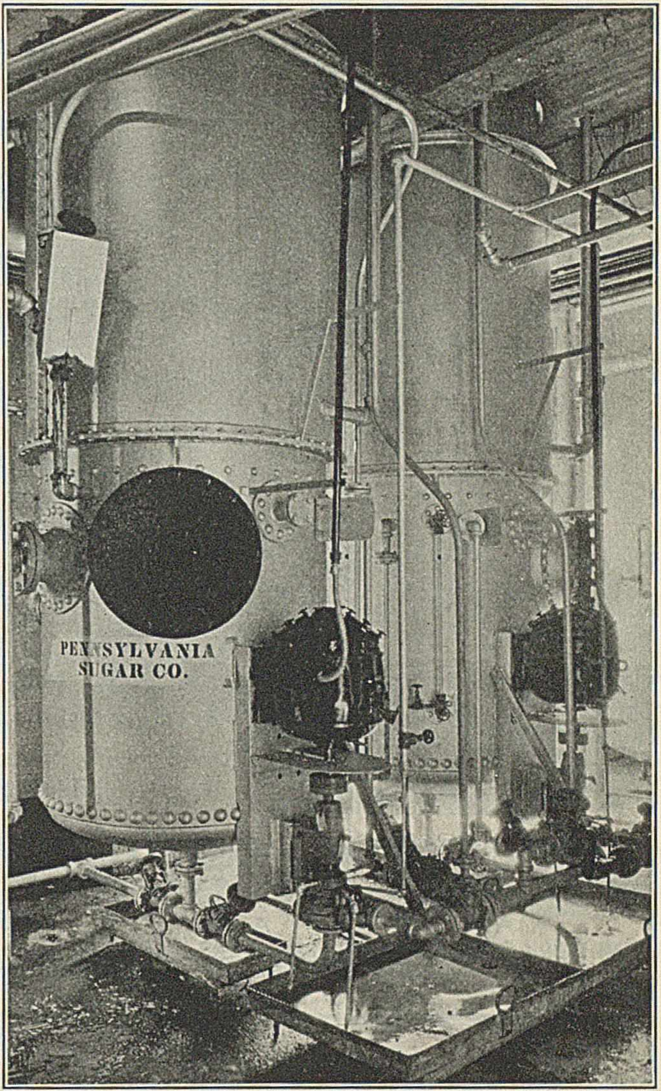
THE PHYSIOLOGIST became interested in nucleic acids when it was found that their derivatives are a source of muscular activity and that they are factors in fermentation.

THE PHYSICIAN was the first and the last to devote attention to nucleic acids as the source of uric acid, the cause of gout and other maladies.

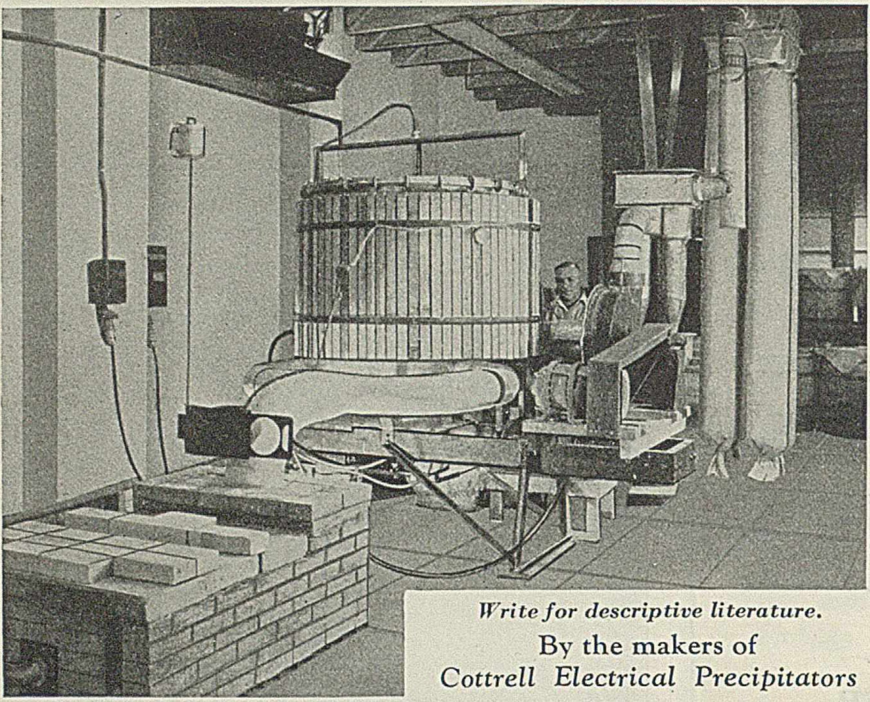
330 Pages Price $4.50

CHEMICAL CATALOG COMPANY, Inc.
419 Fourth Avenue New York, U.S.A.




PENNSYLVANIA
SUGAR CO.

The Peebles - Western Precipitation Company SPRAY DRYER



Write for descriptive literature.

By the makers of
Cottrell Electrical Precipitators

The application of spray drying to industry has been retarded by lack of proper laboratory scale experimental equipment. The ordinary spray dryer consists of a large chamber or flue for hot gases and a central spray for introducing the materials to be dried. When such a dryer is reduced to bring the capacity of the apparatus down to laboratory quantities, the sprayed liquid material is deposited on the chamber walls before it has time to dry. The patented principle of the Peebles spray drying system eliminates this restriction. By suitable arrangements for handling the flow of gases, the droplets from the spray or atomizer are prevented from reaching the walls before the drying is completed

By employment of this principle, the Western Precipitation Company has developed the Peebles laboratory unit shown. The desiccating chamber of this unit is only four feet in diameter whereas the diameter of the smallest commercial Peebles unit is nine feet, and that of other makes is about twenty feet. This laboratory unit is complete with gas furnace, desiccator, multiclone aud bag filter.

While ordinarily from 90% to 99% of the spray dried product in the outlet gases from the desiccator is collected in the Multiclone, the bag filter removes the small remainder and permits discharging directly into the operating room. The evaporating capacity of this laboratory unit is up to 200 pounds per hour. With a 20% feed, it produces 50 pounds of dried product in one hour's operation, while with a 50% feed, the production would be 200 pounds per hour.

The unit is built so that all of its parts are accessible for cleaning, thus avoiding contamination of the dried material from previous runs. The following list of materials that have been successfully dried in the laboratory unit shown indicates the possibilities of this apparatus:

Barium Sulphate
Carbon Black
Lithopone
Calcium Chloride
Coffee Extract
Yeast
Crushed Onions
Lime Sulphur
Zinc Carbonate
Zinc Hydroxide
Zinc Sulphide

WESTERN PRECIPITATION CO. CHEMICAL ENGINEERS

MAIN OFFICE and LABORATORIES—1016 West 9th St., LOS ANGELES, CALIF., U. S. A.
NEW YORK OFFICE and RESEARCH CORP., 405 Lexington Avenue
Chicago Office—RESEARCH CORP., 343 So. Dearborn St.

TROUBLESOME IMPURITIES—

Colloids, dissolved materials, suspended matter, objectionable colors, odors, and tastes which escape separation by other methods of treatment can be removed from your process liquids with surprisingly small percentages of DARCO.

This Trade-mark DARCO On Every Carton

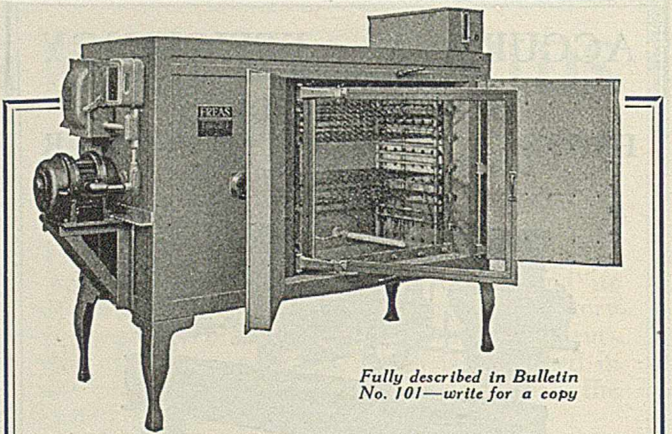
"IT GOES FURTHER"

A free sample and instructions for testing will be furnished on request.

DARCO SALES CORPORATION
45 East 42nd Street
New York, N. Y.

Telephone:
VAnderbilt 3-1592

Cable Address:
DARCOSALE, New York



Fully described in Bulletin No. 101—write for a copy

Weather Conditions
as you want them

HERE is an entirely new type of laboratory cabinet with combined vapor pressure, humidity, and temperature controls—providing facilities for the constant maintenance of these factors, at any required values, from 5° above room to 150° F.; at vapor pressures from 0.5 up to 4.5 inches of mercury above atmospheric pressure—permitting studies and observations to be made under controlled atmospheric conditions. Entirely automatic self-contained units—they are applicable for drying and baking operations—to control the rate of evaporation; for biological investigations where an environmental control is required; as an accelerated aging cabinet for testing paints, foodstuffs, and other materials; as a fermentation and proofing cabinet for flour testing; for incubation, and other purposes that will suggest themselves, which necessitate the precise control of atmospheric elements. Further details, on request.

FREAS THERMO-ELECTRIC COMPANY
1211 SOUTH GROVE STREET
IRVINGTON, N. J.

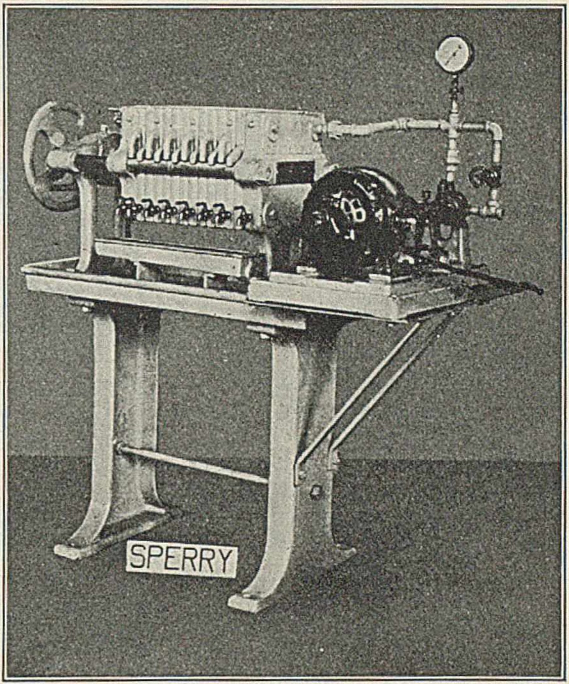
LABORATORY FILTER PRESS

FOR EXPERIMENTAL OR SMALL BATCH OPERATION

◆

The small Filter Press shown is equipped with Motor Driven Pump with Pressure Regulating By-Pass and Mounted on Drained Cast Iron Table.

Arranged for Washing and for Open or Closed Discharge.



LABORATORY FILTER PRESS

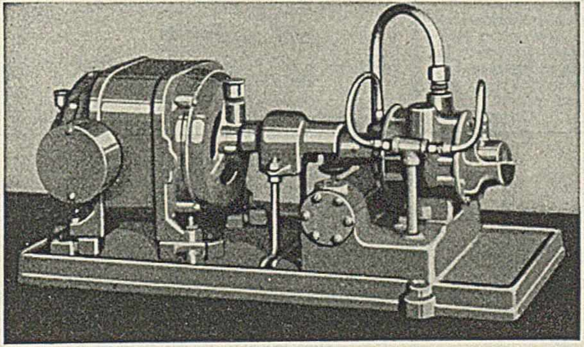
New York, H. E. Jacoby
205 E. 42nd St.

D. R. SPERRY & CO., BATAVIA, ILL.

San Francisco, Cal., B. M. Pilhashy
Merchants Exchange Bldg.

SPERRY FILTER PRESSES

LAMMERT VACUUM-OR-PRESSURE PUMPS



JUST LIKE VACUUM OR PRESSURE FROM A BIG RESERVOIR

Lammert Vacuum-or-Pressure Pumps exhaust or compress air or gas with a uniform, irresistible, non-pulsating flow—just the same as if used in connection with a big reservoir.

The rotary action makes very close clearances possible—minimizes slippage—insures full capacity at high vacuum (30 microns).

These pumps, due to the rotary principle and the fact that wear is automatically taken up, maintain their high initial capacity permanently.

Write for descriptive catalog today.

LAMMERT & MANN COMPANY
217 N. Wood Street Chicago, Ill.

EQUILIBRIA AND RATES OF SOME ORGANIC REACTIONS

by James B. Conant
Chairman of the Division of Chemistry
Harvard University

A knowledge of the structural formula of an organic compound enables an experienced organic chemist to make a surprising number of accurate predictions. He is, however, in a less satisfactory position when it comes to predicting the energy changes involved in the transformation of the substance into other compounds or the rate of its reactions. The author illustrates in this pamphlet certain aspects of the general problems involved by a consideration of some of the quantitative studies which he and others have been conducting at Harvard University during the past ten years. This publication is one of the Charles Frederick Chandler Fund Lectures on chemistry, $0.50, including portrait, tables and diagrams.

COLUMBIA UNIVERSITY PRESS
2960 Broadway, New York, N. Y.

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.

Specialist in the Utilization of Natural Resources, the Elimination of Waste and the Recovery of By-products

Complete Chemical and Food Producing Plants Constructed and Operated

---

GUSTAVUS J. ESSELEN

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 Metallurgical Patents and Applications Involving Processes and Products.

Ex-Examiners in Chemical Divisions,
U. S. Patent Office

726 9th St. 414 Marine Bank Bldg.
Washington, D. C. Houston, Texas

FROEHLING & ROBERTSON, INC.

Established 1881

Inspection Engineers and Chemists

Richmond, Va. New York, N. Y.

ISMAR GINSBERG, B.Sc.Chem.Eng.

Expert Service on Uses of
Chemicals, Raw Materials,
Manufactured Products, etc.
Also Translations—Patent Searches—
Literature Reviews—Bibliographies

33 W. 42nd St. New York

RUSSELL F. HECKMAN

Analytical and Consulting Chemist

Petroleum Products, Fuels, Metals, Alloys, Ores, Foodstuffs, Waters, Soils, Agricultural Materials, Assaying, Corrosion Problems and Surveys.

1118 Nineteenth Street Denver, Colorado

Homogeneous Laboratory of the

HOMOGENEOUS EQUIPMENT CO.

Specialists in Corrosion Problems
Protective Metallic Coatings
Homogeneous Lead and Pure Block Tin Linings
Patents Investigated
Consulting, Testing, Developing.

Francis R. Glenner, Chemical Engineer
Office—1569 Ocean Ave., Brooklyn, N. Y.
Laboratory—Greenpoint, Brooklyn, N. Y.

Dr. Walter Cross Dr. Roy Cross

KANSAS CITY TESTING LABORATORY

Chemists—Engineers—Inspectors

700 Baltimore Ave., Kansas City, Mo.

THEODORE G. KENNARD, Ph.D.

Chemical Spectral Analysis

Geochemistry Rare Elements

117 E. 7th St. Claremont, Calif.

MEIGS, BASSETT & SLAUGHTER

Incorporated

"From Research to Plant in Operation"
Chemical Engineers

Research—Design—Engineering
Reports on Projects for Financing

Drexel Building Philadelphia

W. FAITOUTE MUNN

Chemist—Microscopist
Photomicrography

Color transparencies
Chalk control tests
Research & Investigation

Photomicrographs and Lantern slides of commercial products for patent litigation, for advertising purposes and control.

318 White St. Orange, N. J.

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.

SIRDEVAN CHEMICAL ENGINEERING CO. INC. (1930)

D. F. Sirdevan B.Sc. Pres.

Consulting Designing
Engineering Development

Mineral Acids Heavy Chemicals
By-Products Recovery

Specializing in Contact Process
Sulphuric Acid Manufacture

818 Reisch Bldg. Springfield, Illinois

Tel. Main 6208

HENRY FIELD SMYTH, MD.,Dr.P.H.
HENRY F. SMYTH, Jr., B.S. in Ch.E., M.S.

Consultation and Investigations in Public Health, Industrial Hygiene, Toxic Hazards in Industry, Bacteriological Processes, Spoilage, and Bacteriological Troubles.

307 N. Wayne Ave., 34th and Locust Sts.
Wayne, Pa. Philadelphia, Pa.

FOSTER D. SNELL, INC.

Chemists—Engineers

A technical organization offering complete consulting, research, operating and management service.

130 Clinton Street Brooklyn, N. Y.

---

117 E. 7th St. Claremont, Calif.

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. Patent Services.

Nicholas Road Dayton, Ohio

THE WESTPORT MILL

Westport, Conn.

Laboratories and Testing Plant of
THE DORR COMPANY

Chemical, Industrial and Metallurgical Engineers

A. W. WILLIAMS INSPECTION COMPANY

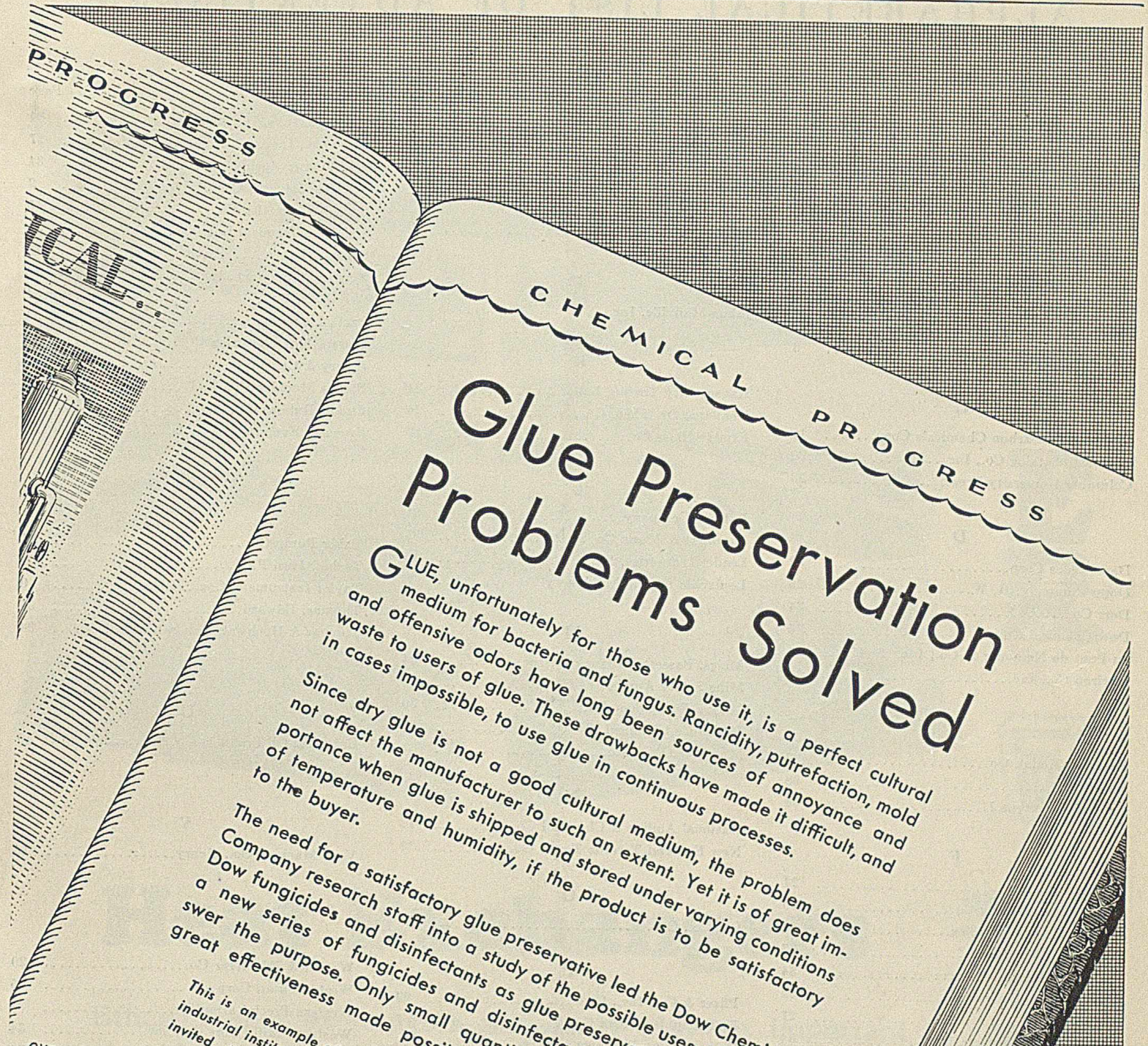
Specializing in the Inspection of

POLES, PILING, CROSSARMS, CROSS TIES, CONDUIT, LUMBER, STRUCTURAL TIMBER and PRESERVATIVE TREATMENTS

Analysis of Wood Preservatives

MOBILE, ALABAMA

Inspectors for Assignments at All Plants



CHEMICAL PROGRESS

Glue Preservation Problems Solved

GLUE, unfortunately for those who use it, is a perfect cultural medium for bacteria and fungus. Rancidity, putrefaction, mold and offensive odors have long been sources of annoyance and waste to users of glue. These drawbacks have made it difficult, and in cases impossible, to use glue in continuous processes.

Since dry glue is not a good cultural medium, the problem does not affect the manufacturer to such an extent. Yet it is of great importance when glue is shipped and stored under varying conditions of temperature and humidity, if the product is to be satisfactory to the buyer.

The need for a satisfactory glue preservative led the Dow Chemical Company research staff into a study of the possible uses of various Dow fungicides and disinfectants as glue preservatives. Dowicide, a new series of fungicides and disinfectants, was found to answer the purpose. Only small quantities were required, yet its great effectiveness made possible large savings to glue users.

This is an example of the cooperation of the Dow research division with industrial institutions to prevent waste and aid production. Your inquiry is invited. Ask for bulletin 19, "Recent Developments in Glue Preservation."

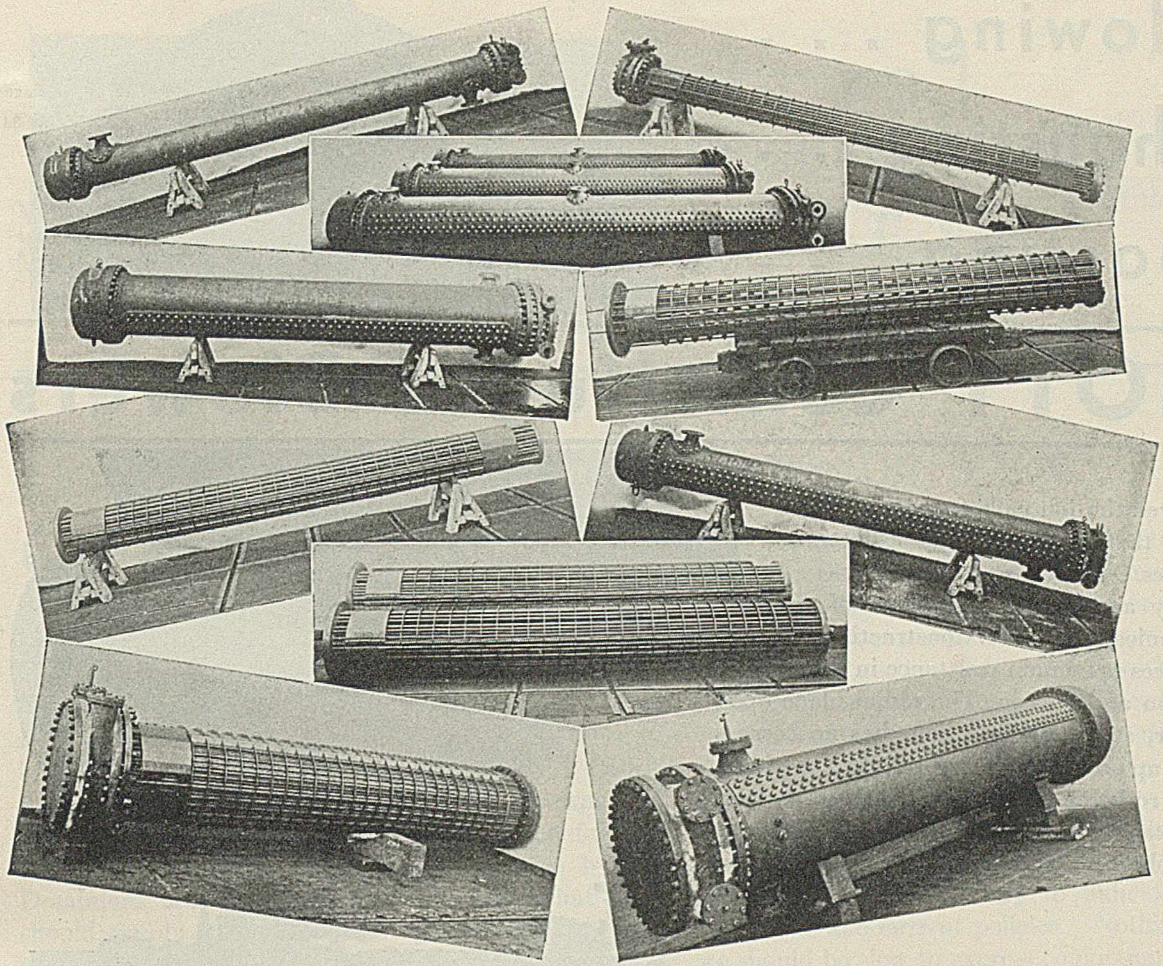
OVER 200 PRODUCTS CARRY THE DOW

DOW

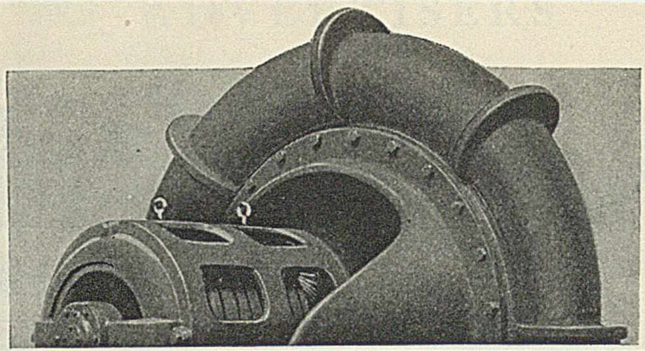
TRADE MARK

THE DOW CHEMICAL COMPANY . . . MIDLAND, MICHIGAN

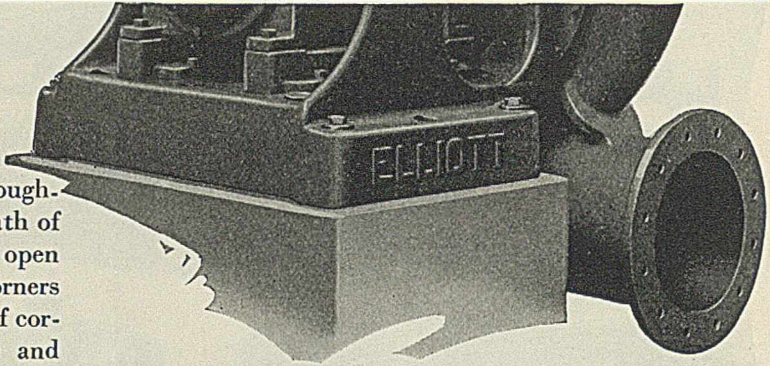
ALPHABETICAL LIST OF ADVERTISERS



For blowing . . .
exhausting . .
boosting . . .

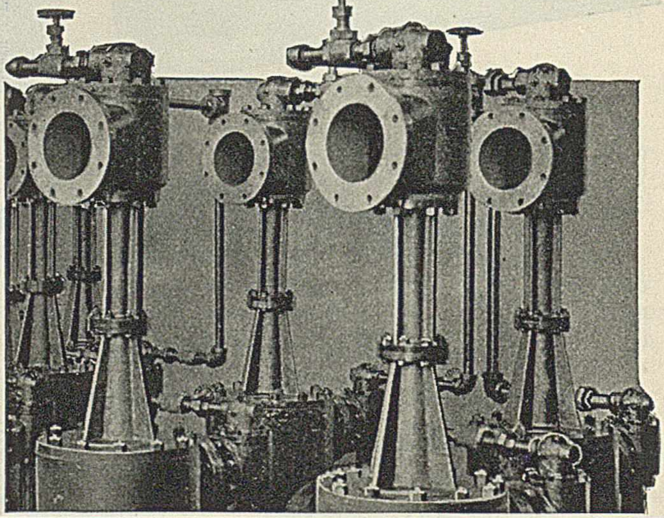


ELLIOTT Centrifugal Blowers

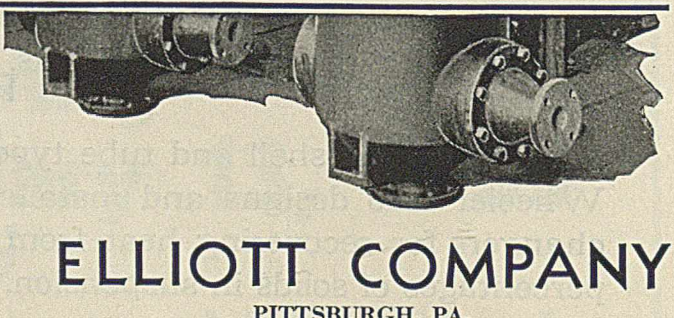


Wherever the job calls for a "real" blower, that is the place for Elliott machines. Their construction is particularly adapted for the needs of the chemical industries. Construction throughout places maximum resistance in the path of corrosion and erosion. The radial blade open impeller, strong and efficient, has no corners to clog up and its form permits the use of corrosion resisting materials. Single-stage and multi-stage types for a wide range of pressures and volume capacities. Write for bulletin.

For creating
vacuum for
industrial
processes . . .



ELLIOTT Steam Jet EJECTORS



Today vacuum processing is coming into its own. Vacuum operation is creating economies and improving products due to lower temperatures in such processes as distillation, evaporation, deodorization, dehydration, refrigeration, etc. Elliott ejectors make vacuum processing economical, and Elliott engineers have the necessary knowledge to apply ejectors properly. If you haven't investigated the use of vacuum in the manufacture of your product, let us go into the subject with you.

G-303

ELLIOTT COMPANY
PITTSBURGH, PA.
Heat Transfer Dept. . . . JEANNETTE, PA.
Centrifugal Blower Department
Suite 506, Morris Building, PHILADELPHIA, PA.
District Offices in Principal Cities

INDUSTRIAL
and Engineering
CHEMISTRY

PUBLISHED BY THE
American Chemical Society

VOLUME 25, 1933

Editor: H. E. HOWE

Assistant to Editor: N. A. Parkinson

MACK PRINTING COMPANY
EASTON, PA.
1933