CHEMICAL ENGINEERING SERIES

MATERIALS OF CONSTRUCTION FOR CHEMICAL PROCESS INDUSTRIES

McGRAW-HILL CHEMICAL ENGINEERING SERIES

THE SERIES

BADGER AND BAKER—*Inorganic Chemical Technology*
BADGER AND McCABE—*Elements of Chemical Engineering*
CLARKE—*Manual for Process Engineering Calculations*
DAVIS—*Chemical Engineering Nomographs*
DODGE—*Chemical Engineering Thermodynamics*
EDWARDS, FRARY, AND JEFFRIES—*The Aluminum Industry (in Two Volumes): Aluminum and Its Production; Aluminum Products and Their Fabrication*
GRISWOLD—*Fuels, Combustion, and Furnaces*
GROGGINS—*Unit Processes in Organic Synthesis*
HUNTINGTON—*Natural Gas and Natural Gasoline*
KIRKBRIDE—*Chemical Engineering Fundamentals*
LEE—*Materials of Construction for Chemical Process Industries*
LEWIS AND RADASCH—*Industrial Stoichiometry*
MANTELL—*Adsorption*
MANTELL—*Industrial Electrochemistry*
NELSON—*Petroleum Refinery Engineering*
PERRY (EDITOR)—*Chemical Engineers' Handbook*
PIERCE—*Chemical Engineering for Production Supervision*
RHODES, F. H.—*Technical Report Writing*
RHODES, T. J.—*Industrial Instruments for Measurement and Control*
ROBINSON AND GILLILAND—*Elements of Fractional Distillation*
SCHMIDT AND MARLIES—*Principles of High-polymer Theory and Practice*
SHERWOOD—*Absorption and Extraction*
SHERWOOD AND REED—*Applied Mathematics in Chemical Engineering*
SHREVE—*The Chemical Process Industries*
SMITH—*Introduction to Chemical Engineering Thermodynamics*
TYLER—*Chemical Engineering Economics*
VILBRANDT—*Chemical Engineering Plant Design*
WALKER, LEWIS, McADAMS, AND GILLILAND—*Principles of Chemical Engineering*
WILSON AND WELLS—*Coal, Coke, and Coal Chemicals*
WINDING AND HASCHE—*Plastics, Theory and Practice*

CHEMICAL ENGINEERING SERIES

MATERIALS OF CONSTRUCTION FOR CHEMICAL PROCESS INDUSTRIES

BY

JAMES A. LEE
Southwestern Editor of McGraw-Hill Publications
Formerly Managing Editor of Chemical Engineering
and Its Predecessor Chemical and Metallurgical
Engineering

FIRST EDITION
SECOND IMPRESSION

McGRAW-HILL BOOK COMPANY, INC.
NEW YORK TORONTO LONDON
1950

MATERIALS OF CONSTRUCTION FOR CHEMICAL PROCESS INDUSTRIES

PREFACE

Chemical engineers, plant superintendents, and foremen—even the operators in process industries—often need to know how to combat corrosion. What material of construction will withstand some particularly corrosive chemical is a common problem. The engineer designing process equipment as well as the fabricator share in this responsibility.

Scattered through literature is a great deal of information dealing with the materials of construction used in the production and handling of corrosive chemicals. Often these articles and reports contain the solutions to problems of corrosion, but because they are scattered, much time and effort are required to find the data most needed at the moment. And it sometimes happens that when the information is located it turns out to be based entirely on laboratory test data. Although these tests are helpful, they seldom duplicate actual plant experience. Furthermore, they may prove misleading because they fail to include lower cost materials that would be just as resistant and more economical in practical use. For this reason, emphasis throughout this book is on materials of construction that have been found by operating experience to be the most serviceable and economical in commercial-size plants.

The author wrote this book to bring together and correlate the information he himself often needed and found only with the greatest difficulty. It contains information dealing with more than 300 chemicals and combinations of chemicals. Mixtures have been included because their corrosive action cannot always be determined by the behavior of the individual constituents. Corrosion problems encountered in such process industries as foodstuffs, sulphate pulp, soap, synthetic resins, and cane sugar are also discussed. The number that might have been included is almost limitless, but it is believed that those selected will cover the majority of cases where chemical corrosion is an important problem.

A table of contents has not been included, for each chemical or combination of chemicals is treated as a "chapter." The individual chemicals appear in alphabetical order. The combinations are listed according to the predominating chemical constituent.

Each chapter generally opens with a brief introduction followed by sections on (1) production, (2) handling, and (3) packaging. The first section is subdivided into a brief discussion of the metallic and nonmetallic materials used in production. This is followed by a description of the process in which the materials used for the construction of each piece of equipment are brought out whenever possible. The second section is concerned with the corrosiveness of the chemical when it is being used as a finished product, or as a raw or intermediate material in the production of some other chemical or product. And, of course, the section on packaging deals with materials of construction that are being used for shipping containers.

While this plan has been followed for most chemicals, it has not always been possible or advisable to do so. No attempt has been made to include every process used for making every chemical. In some cases the information is not available for publication. In others, the process is known but no up-to-date account of construction materials is available. Obsolete methods are purposely omitted.

As far as is practical the use of trade names has been avoided. Where they do appear, their chemical compositions are tabulated at the back of the book. So are the compositions of the type-numbered stainless steels.

For over 20 years the author has been closely associated with developments in this general field. He has accumulated extensive files of information published by engineers and other workers covering their experience with construction materials in commercial chemical plants. Upon these files he has depended for much of the information in this volume. It has been supplemented by some heretofore unpublished material.

Literature references are included for those readers who may be interested in having the text amplified and extended. Consequently, although most of the references are appended to a specific point in the text, they generally cover not only that particular feature but often much of the whole process being described.

Most of the published information on which the author has drawn was taken from *Chemical Engineering* and its predecessor, *Chemical and Metallurgical Engineering*. Many of the flow sheets first appeared in *Chemical and Metallurgical Engineering*'s Chemical Engineering Flow Sheets. The author of this book has merely added the materials of construction generally used for each essential piece of equipment in the particular plant on which the flow sheet is based. Grateful acknowledgment is made for permission to use these diagrams. Among the other publications that have been helpful are *Food Industries*, *Industrial and Engineering Chemistry*, *Chemical Industries*, *Industrial Chemist*, *Ca-*

nadian Chemistry and Process Industries, and *Chemical Engineering Progress.* The reports of the American and British teams of scientists and engineers who visited German chemical plants shortly after the war also proved to be valuable mines of information.

The author desires to thank those engineers in various chemical plants who contributed their own experience to the volume. And last but by no means least, are the following authorities who reviewed the manuscript: Philip S. Barnes of the Pfaudler Company, Junius D. Edwards of the Aluminum Company of America, W. Z. Friend of the International Nickel Company, Percy C. Kingsbury of the General Ceramics and Steatite Corporation, and George A. Sands of Electrometallurgical Corporation.

JAMES A. LEE

EAST ORANGE, N.J.
September, 1950

MATERIALS OF CONSTRUCTION FOR CHEMICAL PROCESS INDUSTRIES

ACETALDEHYDE

Considerable information has been made available about the production of acetaldehyde during the past few years. Almost all the material has concerned German plants, but the processes and probably the materials of construction are similar to those used in this country.

Production

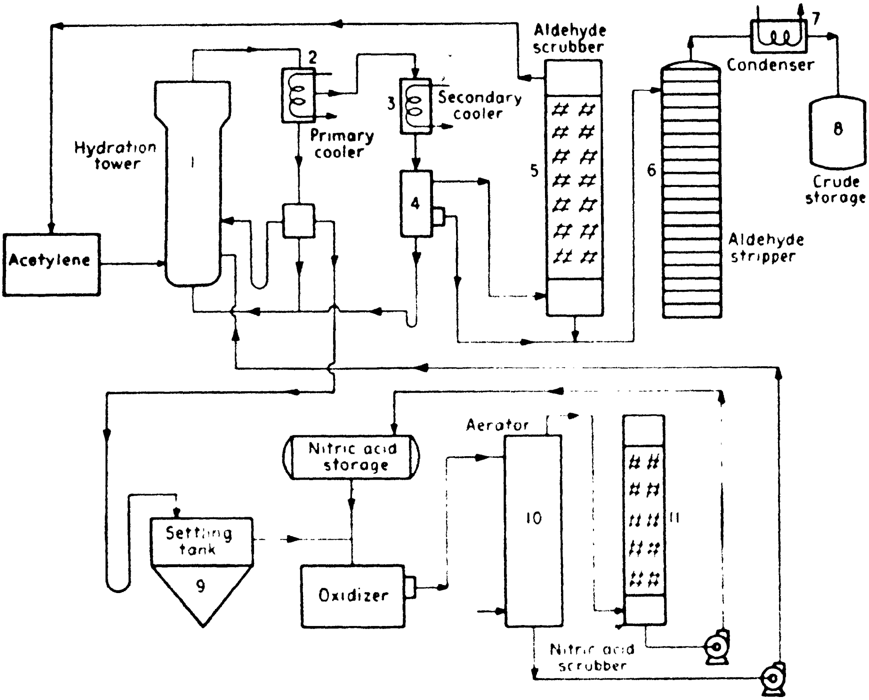
Materials of Construction.—Acetaldehyde is made in several German chemical plants by the direct hydration of acetylene in the presence of mercuric ions. (Brundrit, D., A. W. C. Taylor, and J. F. Ellis, German Acetylene Chemical Industry Acetaldehyde Manufacturing, PB 79186, p. 9, Office of Technical Services, U.S. Department of Commerce.) The hydration of acetylene is carried out in a sulphuric acid solution of mercuric sulphate. For that reason the solution vessels must be protected by acid-resistant linings. The usual method is to use rubber-lined equipment, and because of the scarcity of natural rubber in Germany during the war years, synthetic rubber of the Buna S type had to be used. This material was not so resistant to the operating conditions as was natural rubber, and the most successful lining was acidproof glazed porcelain tiles in double layer in Asplit. Glass-lined steel is suitable too.

In the acetaldehyde-purification process, the solution of acetaldehyde in water is distilled under pressure. The gas is then cooled in a stainless-steel tube and shell cooler. The weak acetaldehyde solution is usually stored in mild-steel tanks. It is distilled by conventional methods, and the final product is pure dry acetaldehyde. The waste water from the first still contains a little acetic acid, and because of this the stills are usually built of stainless steel or of cast iron so thick that corrosion does not matter for some time. High-silicon iron pipe has shown negligible corrosion after 5 years' handling weak acetic acid slop from the column.

At the Wacker Werke, Burghausen, the hydration vessels have mild-steel towers lined with natural rubber. In the gas cooling system, due to the small carry-over of catalyst spray and to the presence of small quantities of acetic acid, the primary condensers are made of Type 316 stainless steel. The secondary condensers are made of mild steel. The acetaldehyde water scrubbing towers are mild steel, and the packing is slats of wood.

At Wacker's, Burghausen, the preheaters on the feed to the main columns are

Type 317 stainless steel and Remaint 1710S (Cr, 17, plus Mo) tubes. In the main still there is a Type 317 stainless-steel tube and shell reboiler. The still boiler is Type 317 plated steel, which replaced cast iron. Cast-iron columns are used. The packing is porcelain Berl saddles. Mild steel is used for the acetylene degassing columns.



Acetaldehyde conversion of acetylene at Schkopau.

1. Rubber-lined mild steel, GR-S-lined mild steel, porcelain-tile lined
2. Stainless steel (Cr, 18; Ni, 8; Mo, 3)
3. Mild steel
4. Stainless steel
5. Lead-lined, stainless steel, mild steel, cast iron, rubber-lined
6. Lead-lined, stainless steel, cast iron, rubber-lined
7. Mild steel
8. Mild steel, aluminum
9. Lead-lined
10. Rubber-lined steel
11. Stainless steel

At Knapsack the hydration vessels have mild steel towers lined with Buna rubber or with two layers of white glazed porcelain tiles set in Asplit. The latter have been in satisfactory service for over 5 years.

Acetylene Hydration Process.—This process is the conventional method using a liquid-phase mercuric sulphate catalyst suspended in an aqueous solution of sulphuric acid and iron sulphate. The operation at Schkopau is the most highly developed. [Boundy, R. H., and R. L. Hasche, Report on Manufacturing of Miscellaneous Chemicals in Plants of I.G. Farben., Combined Intelligence Objectives Committee, G-2 Division, SHAEF (Rear) APO 413, U.S. Department of Commerce.]

Hydration of acetylene is carried out continuously with a liquid catalyst giving 60 per cent conversion per pass and an acetaldehyde yield of 96.5 per cent. Acetylene gas of 97 to 98 per cent purity is introduced in the bottom of the tower. Along with the acetylene, about 1.5 tons per hr. of steam is introduced. The mixture of steam, acetaldehyde, and unconverted acetylene passes from the tower to a stainless-steel cooler, where the temperature is reduced to 60°C. Condensed steam and mercury are returned to the column. The mixture then passes to a stainless-steel cooler where the temperature drops to 25°C. Mercury is returned to the tower, and the condensate, which contains 9 per cent acetaldehyde, is mixed with the absorbing water leaving the scrubbing tower. The acetylene-gas mixture containing acetaldehyde vapor passes up through the scrubber countercurrent to water for recovery. A solution with a 9 per cent concentration of acetaldehyde passes to a stripping column, where acetaldehyde is recovered using live steam for heating.

The scrubbing and recovery system consists of three sets of lead-lined columns, each with an absorber and stripper. The stripping column operates under sufficient pressure to allow condensation of the acetaldehyde solution which has 80 per cent concentration in water and also contains dissolved acetylene.

Acetylene is removed from the top of the primary distillation columns and passes back to the conversion system, while acetaldehyde is taken off at the bottom. A final distillation column recovers acetaldehyde of 99.5 purity.

A portion of the catalyst solution from the hydration tower is continuously withdrawn for regeneration. It passes first to a separator which is lead lined. Mercury sludge settles to the bottom and overflows mixes with a stream of 20 per cent nitric acid, and passes into the oxidizer maintained at 98°C. From there it overflows into a rubber-lined steel column packed with raschig rings. The nitric oxide is stripped out, mixed with air, and absorbed in a second tower.

Packaging

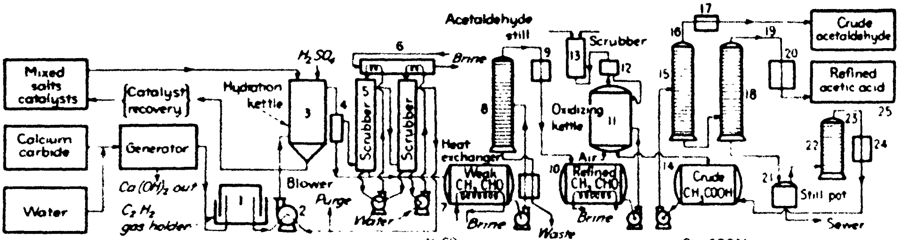
Acetaldehyde is shipped in steel or aluminum drums.

ACETIC ACID

Acetic acid can be produced by any one of several processes and from any one of several raw materials. The amount of acetic acid that is made by hardwood distillation has decreased in recent years. The larger amount of acetic acid is made by synthetic processes.

Production

Materials of Construction.—In the past few years, the trend in the acetic acid industry has been away from copper to stainless steel because of the longer life of equipment. With steel prices more or less stationary, there is more reason now than heretofore to use stainless steel. This is also more or less true for aluminum, which has become more popular for making and handling acetic acid, especially at high temperatures. The oxidation of acetaldehyde to form acetic is carried out in aluminum-lined heat exchangers functioning as reflux condensers. (Aluminum Research Laboratories, unpublished data.) Condensed vapors contain 20 per cent acetaldehyde and 80 per cent acetic. Where a very pure product is demanded, silver equipment is often used owing partly to the clearance of colored substances, even if some contamination by silver does occur. The pharmaceutical grade of acid is often stored in glass-lined tanks. Inconel condenser tubes are used for condensing acetic vapors where a brine is used for cooling.



$CaC_2 + H_2O \longrightarrow CH \equiv CH + Ca(OH)_2$ $CH \equiv CH + H_2O \xrightarrow[Hg\ salts]{H_2SO_4} CH_3CHO$ $CH_3CHO + \frac{1}{2}O_2 \xrightarrow{CH_3COOMn} CH_3COOH$

Acetic acid from carbide.

1. Steel
2. Steel casing, stainless rotor
3. High-silicon iron
4. Type 316 stainless steel
5. Steel and cast iron
6. Steel
7. Steel
8 Cast iron
9. Copper
10. Steel
11. Aluminum-lined steel
12. Aluminum, Type 316 stainless steel
13. Steel
14. Aluminum
15. Copper, aluminum bronze, Types 316, 317 stainless steel
16. Copper, aluminum
17. Copper, aluminum
18. Copper, aluminum bronze, Types 316, 317 stainless steel
19. Aluminum
20. Aluminum
21. Cast iron, copper
22. Copper, aluminum bronze
23 Copper
21. Copper
25 Aluminum

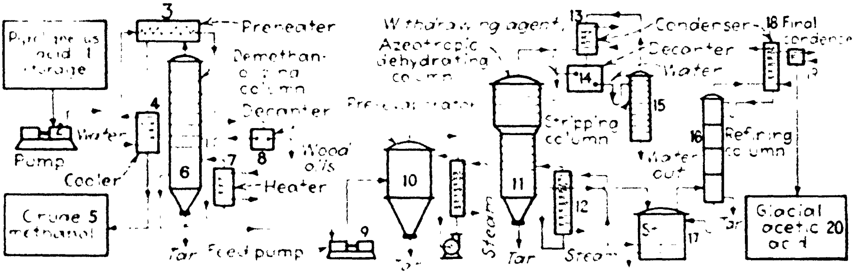
Oxidation of Acetaldehyde Process.—The process and equipment used at Bunawerke, Schkopau, have been reported. (Wood, W. L., Production of Acetaldehyde, Acetic Acid, Acetic Anhydride, and Acetone from Acetylene, Final Report 75, Item 22, British Intelligence Objectives Sub-Committee, His Majesty's Stationery Office, London.) The oxidizers consist of aluminum sections separated by silicon-aluminum alloy rings, together with water-cooling coils. The aldehyde is pumped into the base of the oxidizer from an aluminum tank by a silicon-aluminum-alloy centrifugal pump. The manganese acetate catalyst is fed into the aldehyde feed tank. The gas leaving the column head is passed through a warm condenser consisting of an aluminum tube.

The liquid leaving the top of the vaporizer contains 2 to 3 per cent acetaldehyde and flows to a high-silicon iron-packed column. The packing is porcelain rings. Aldehyde is taken off this still as an overhead product and flows to the base of the oxidizer, the condenser and cooler being of copper. There is a high-silicon iron capacity vessel offset from the base of the column, where vapor disengages from the liquid leaving the heater, which is alongside this vessel. The heater is made of stainless steel.

The liquid from the capacity vessel flows to a high-silicon iron pot, containing a silver coil for heating by indirect steam. The life of this coil is stated to be 2 years. Vapor passes up a high-silicon iron column, which has a copper condenser and cooler giving acetic acid of 98.5 to 99 per cent purity. Storage is in aluminum tanks.

In America stainless-steel reaction vessels are preferred, although copper is sometimes used when a manganese catalyst is employed. Condensers are aluminum. These same plants use aluminum storage vessels except for pharmaceutical-grade acid, when glass-lined tanks are used. Dilute acid is handled by all-bronze, stainless-steel, or Monel pumps. Concentrated acid is handled by stainless steel, aluminum, or Monel.

Azeotropic or Othmer Distillation Process.—In the Othmer process, vapors formed by the condensation of the wood are condensed and the non-condensable gases are discharged from the condenser. This pyroligneous liquor



Acetic acid (Othmer process) from wood distillation.

1. Wood
2. Bronze
3. Copper with copper. Herculoy, or Everdur tubes
4. Copper
5. Carbon steel
6. Copper with bronze caps, etc.
7. Copper with copper. Herculoy, or Everdur tubes
8. Copper
9. Bronze
10. Copper with copper. Herculoy, or Everdur tubes
11. Copper with bronze caps, etc.
12. Copper with copper. Herculoy, or Everdur tubes
13. Copper with copper. Herculoy, or Everdur tubes
14. Copper
15. Copper with bronze caps, etc.
16. Copper with bronze caps, etc.; Type 316 stainless steel
17. Copper with copper. Herculoy, or Everdur tubes; Type 316 stainless steel
18. Copper with copper. Herculoy, or Everdur tubes; Type 316 stainless steel
19. Type 316 stainless steel or silver
20. Aluminum

goes to wood settling tanks. Insoluble tars settle out and are removed. The remainder of the liquor is passed to a copper distilling column where the methanol, acetone, methyl acetate, and other volatile constituents are fractionated off the top as "crude methanol."

The dealcoholized liquor running from the base passes to the preevaporator. This is simply an evaporator with long external tubes, and in this unit the remaining volatiles, acetic acid and water, are distilled away from the tar materials. These tars are largely removed as a residue from the bottom. Vapors on their way to the copper dehydrating column pass through a catchall.

Acetic acid on reaching the base of the dehydrating column is free not only of water (above 99.5 per cent strength) but also of entrainer, a fixed amount of a water-insoluble liquid such as butyl acetate, and thus this single column accomplishes a separation of water containing only 0.01 per cent acid from acid containing less than 0.5 per cent water. This mixture does, however, contain an amount of tar oils which were steam distilled from the preevaporator into the dehydrating column. These oils have a high boiling point and can be removed by a subsequent fractionation. The liquid therefore passes to the copper or stainless-steel acid column, which removes the acetic acid as the low boiler at the head and the tar at the base.

The acetic acid is finally condensed in Type 316 stainless steel or silver and stored in an aluminum tank.

Liquid-Liquid Extraction Process.—Ether extraction has been called the "Brewster process" for T. J. Brewster, who did some early work on it. The development and design by J. M. Coahran (U.S. Patents 1,686,452, Aug. 14, 1928; 1,784,270, Feb. 9, 1930; 1,845,128, Feb. 16, 1932; 1,845,129, Feb. 16, 1932; 1,865,887, July 5, 1932; 1,870,834, Aug. 9, 1932; 2,197,069, Apr. 16, 1940) of new extractors to increase yield and effect other improvements made the process practical.

Settled raw liquor (pyroligneous acid) after settling out of the insoluble tar is fed continuously to a primary still for distillation from the soluble tar in order to lessen fouling of subsequent operations.

Mixed vapors from this still are passed to the heater tube bundle of the evaporator and, after partial condensation, to the middle of the methanol column as its feed. Eighty-five per cent crude methanol is the overhead from this column, and dealcoholized liquid is the bottom discharge. The latter is cooled and pumped through a vent scrubber into the upper part of the mechanical countercurrent extractor.

The acetic acid in the dealcoholized liquor is extracted cold as the aqueous liquid passes downward in this mechanical extractor, using 2.6 volumes of ether per volume of liquor, countercurrent to the rising ether. The ether-saturated extractor liquor is conducted through a heat exchanger to the top of a steam-heated ether exhauster column for the recovery of the dissolved ether. The spent liquor flows from the bottom of this exhauster through the heat exchanger to waste, containing less than 0.1 per cent acetic acid.

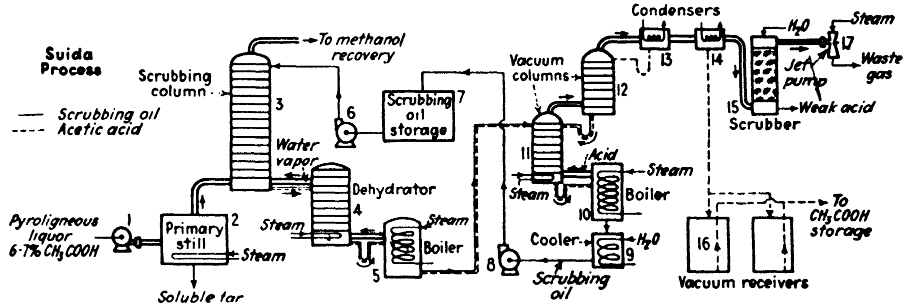
The ether solution of the acetic acid (2 to 3 per cent) is piped from the top of the mechanical extractor to the ether evaporator. Here, heated by the vapors from the primary still, the ether is vaporized, along with some acetic acid.

The acid freed of most of its ether is led to a lower section of this same ether column. The overhead is rectified ether vapor to be condensed and recirculated. The discharged acid collects in an acid-extract receiver kept sufficiently warm by steam to remove ether.

The ether carries over into this acid extract practically all the acetic acid, a small amount of wood oils, some polymerized tar, and from 2 to 3 per cent water—resulting in a 70 per cent dark crude acid. The water content is a distinct advantage, as it forms minimum boiling mixtures with the volatile impurities and facilitates thin fractional separation. If sufficient water is not present, it should be added. The 70 per cent crude acetic can be refined by either continuous or batch distillation.

Final acid condensers are usually constructed of silver, though aluminum or high-silicon iron can be and sometimes is used. Other acid-handling equipment is made of copper or copper alloy, and the parts handling strong hot acid are often lined with acidproof brick set in acidproof cement. Strong acid is stored in aluminum or wooden tanks, with an occasional rubber-lined vessel.

Suida Process.—In the Suida process the upper layer from the initial settling of the crude pyroligneous acid is first treated to remove acetic acid by



Acetic acid from pyroligneous liquor.

1. Bronze
2. Copper, with copper, Herculoy, or Everdur tubes
3. Copper, with copper, bronze, Herculoy, or Everdur caps, etc.
4. Copper, with copper, Herculoy, or Everdur caps, etc.
5. Copper, with copper, Herculoy, or Everdur tubes
6. Bronze
7. Wood or copper
8. Bronze
9. Copper, with copper, Herculoy, or Everdur tubes
10. Copper, with copper, Herculoy, or Everdur tubes
11. Copper, with copper, bronze, Herculoy, or Everdur caps, etc.
12. Copper, with copper, bronze, Herculoy, or Everdur caps, etc.
13. Copper, with copper, Herculoy, or Everdur tubes
14. Copper, with copper, Herculoy, or Everdur tubes
15. Copper, with ceramic raschig rings
16. Copper or Type 316 stainless steel
17. Bronze or Type 316 stainless steel

being vaporized and scrubbed countercurrently with a wood oil, which is obtained by vacuum distillation of the tar from the settlers. (Poste, Suida Process for Acetic Acid Recovery, *Ind. Eng. Chem.*, Vol. 24, p. 722, 1932; and Shreve, R. N., "The Chemical Process Industries," McGraw-Hill Book Company, Inc., New York, p. 685, 1945.) The oil with acetic acid in solution passes through a dehydrating column into a vacuum stripping column, where the acetic acid is boiled off under vacuum. The oil returns to the system, while the acetic acid is rectified to 92 per cent or higher. Fresh oil is added to the scrubbing column at frequent intervals. Vapors from the scrubbing column, having been stripped of acetic acid by the oil, are sent to methanol recovery, their alcohol content being 4 per cent. They also contain a small amount of acetone. Subsequent concentration in an exhausting and rectifying system produces 90 per cent methanol or its equivalent. Final rectifying yields 99 per cent methanol, allyl alcohol, acetone, and "weak alcohol."

Oxidation of Ethanol Process.—In the liquid-phase oxidation of ethanol by the quick-vinegar process the presence of mycoderma aceti is used to convey oxygen to the alcohol and effect oxidation. (Groggins, P. H., "Unit Processes in Organic Synthesis," McGraw-Hill Book Company, Inc., New York, 3d ed., p. 448, 1947.) In the early practice of the process wooden tanks filled with beechwood shavings were used. A dilute alcohol solution is allowed to trickle down over the packing material. Oxygen or air introduced at the bottom of the vat becomes heated from the heat of the reaction, rises, and passes off at the top. The product consists of a dilute acetic acid. More modern practice calls for chemical-stoneware towers filled with beechwood shavings.

Handling

Wood.—This material of construction has long been used for equipment for producing and handling acetic acid. Although it has been replaced by other materials in modern plants, wooden storage and process tanks and other equipment are still in use in many plants and processes.

Stainless Steels.—The trend in the several branches of the acetic acid industry is toward the greater use of stainless steels. Construction materials of regular types of stainless steel, especially those containing molybdenum, can generally be used to handle all concentrations at normal temperatures. Under some conditions certain of these steels can also handle acetic acid at elevated temperatures. These materials, however, are not highly resistant to acetic acid at the boiling point or to acetic vapor.

For conditions involving the higher concentrations at high temperature, and where purity of the product is an important factor, the highly alloyed stainless steels or other high alloys should be used. Such alloys as Worthite and Durimet are used extensively for pumps and valves. The Hastelloys are appreciably affected by temperatures at or above the boiling point. Equipment made of Hastelloys B and C, which are especially resistant, can handle all concentrations of acetic acid at all temperatures and acetic anhydride, with a loss of less than

1 mil per year. These alloys, however, can be economically used only where chemicals other than straight acetic acid are present.

Copper.—By and large, copper was the premier metal of the acetic acid industry and still is used to a very large extent. Corrosion of copper by acetic acid can be controlled to a considerable extent. Corrosion is accelerated by the presence of air, as is evidenced by the fact that leaky equipment is always short-lived. By the same token, the equipment used in a continuous process will last much longer than if used intermittently, as in a batch process.

According to one authority (Albin, T. C., Acetic Acid, *Chem. & Met. Eng.*, Vol. 41, No. 10, p. 514, 1934), the next most important factor affecting the corrosion of copper is its hardness, hence the once universal practice of "hand hammering" all copper equipment. To an unfortunate extent, however, that process is becoming a lost art, presumably because to most people it seems an economic waste to allow a high-priced man, such as a coppersmith, to peck away for hours on a section of a distilling column after it is, to all appearances, completely fabricated. Experience has shown that the hours spent in proper hammering give months of added service.

Annealed spots in copper equipment, where connections are brazed on without proper rehammering, are attacked much more rapidly than is the surrounding hard metal. There is enough difference between the hard and soft copper to set up electrolysis, with the result that the soft metal is dissolved and then deposited on the adjacent hard metal as firmly attached copper "warts." By giving thought to this feature in the design of equipment, the number of "soft spots" can often be reduced. In inaccessible places, where these soft spots cannot be reached with a hammer, a liberal coating of silver solder, extending well over onto the hard metal, will materially retard corrosion.

Although it conflicts to some extent with the corrosion tests reported by the bronze manufacturers, experience has been that copper is more resistant than any of its alloys. However, phosphor bronze of a composition of 95 per cent Cu, 4.8 per cent Sn, and 0.2 per cent P has been found quite satisfactory. It makes sound castings and is not difficult to machine. It can be brazed as easily as copper without developing shrinkage cracks on cooling. Thus it is very easy to repair phosphor-bronze equipment by the same methods used on copper apparatus.

Copper equipment is employed to a very considerable extent in the manufacture of acetic acid by the several processes in common use. Examples include vessels for the treatment of calcium acetate with sulphuric acid and for the production synthetically from acetylene involving the intermediate formation of acetaldehyde. In the latter process aluminum bronze has been used to a large extent for stills and columns.

Aluminum-bronze castings have been used to a considerable tonnage in acetic acid applications. (Othmer, D. F., Guarding Against Corrosion in Acetic Acid Equipment, *Chem. & Met. Eng.*, Vol. 39, No. 3, p. 136, 1932.) On the whole, the results have been very satisfactory. Large distilling plates, as well as pumps for handling up to 2,000 gal. per min., have been made of this material. Cast-aluminum-bronze pipe has been available for use with acetic acid but is not often used.

Aluminum.—This metal is preferred for high-temperature conditions, as in stills and condensers. Acetic acid in concentrations up to between 98 and 99.5 per cent can be handled at any temperature below the boiling point. Aluminum is only slightly attacked by strong acid. The rate is higher as the dilution increases; however, even at boiling temperatures, attack by glacial acetic is of a very low order. Also, the rate of attack is accelerated by impurities in the weak acid. The presence of air does not have the same adverse effect on aluminum that it has on copper. Accordingly, this metal is more satisfactory for product lines, blow cases, storage tanks, and other equipment that is used intermittently. Aluminum equipment consisting of condensers, pipe, valves, and receivers is also used to handle glacial acetic acid. Aluminum tanks are used for the storage of acetic acid at temperatures up to 80°C.

Of particular importance is the fact that acetic acid can be handled without danger of discoloration. Therefore, "water whiteness" of acetic acid and products made from acetic acid is assured by use of aluminum.

Silver.—This metal is recommended as a material of construction resistant to corrosive attack by acetic acid in all concentrations and at all temperatures. (Burman, L. C., Silver, *Chem. Eng.*, Vol. 53, No. 11, p. 262, 1946.) Excess oxygen in the solution has no effect upon the resistance of the silver to such attack. A feature of silver in organic operations is that many of the silver organic compounds are colorless and therefore not objectionable should small quantities contaminate the product.

Apart from the use of silver for its corrosion resistance are the superior heat-transfer qualities and the ease of fabricating complicated shapes. Coil and tubular condensers and heat exchangers are successfully used against acetic acid corrosion. At pressures beyond which solid silver or silver alloys cannot be used economically because of the weight of metal required for mechanical strength, silver-clad materials are available and in use. Two types of cladding are in general use. One involves the use of high pressure and heat for a metal-to-metal bond between silver and a base metal. The other involves fitting silver or silver-alloy shapes to parts or equipment already fabricated or partially fabricated. In this latter case, the silver liner may be expanded into or drawn tightly over heavy-walled tubing or pipe. Or a tube sheet and its holes may be lined to receive a bundle of tubes clad inside, outside, or on both sides. In general, silver and the silver alloys are readily fabricated into any required shapes for the purpose of protecting base-metal chemical equipment.

Techniques have been developed for the joining of silver-lined tubing with or without flanges. The same is true for tubing clad on the outside or inside and outside, except that these are joined without flanges. These techniques involve the use of silver rings inside or outside the tubing, as required, and silver solders.

Lead.—Acetic acid solutions are moderately corrosive to lead, and it is not generally recommended for handling either dilute or glacial acid where there is agitation, aeration, or high temperature. This rules out the use of lead except as a storage medium where there is slight possibility for removal of the lead acetate film through agitation of the liquid. In a number of cases the amount of lead pickup is sufficient to prohibit the use of lead.

Lead-lined tanks and vats have given good service in many cases where glacial acetic acid has been stored. Precautions to be taken here are that the tanks be closed to exclude circulating air. Satisfactory length of service is usually obtained unless the contents are changed quite frequently, in which case corrosion may become excessive because of the frequency of air changes.

Lead pipe or lead-lined pipe is not recommended for the transfer of liquid acetic acid. In cases where lead pipe has been used, moderate corrosion occurred in the straight sections, but at bends corrosion was rapid to the extent of completely destroying the pipe wall at the point of impingement.

High-silicon Iron.—Its use is not limited by temperature, concentration, purity of acid, or aeration. (Staley, W. D., High-Silicon Iron, *Chem. Eng.*, Vol. 53, No. 12, p. 210, 1946.) High-silicon iron is used extensively in the production of acetic acid by the destructive distillation of wood and extraction with ether or other solvents from the crude pyroligneous liquor. To cite actual installations from high-silicon iron equipment, pipe, fittings, and valves are handling acetic acid vapors in concentrations ranging up to about 80 per cent at temperatures up to 150 to 160°F. In refining the crude acid, similar equipment is used for concentrations up to 99 per cent at temperatures up to 140°. Another case is the use of valves for handling a mixture of 30 per cent acetic acid and 70 per cent propionic acid at a temperature of 150 to 160°F. A more severe application is the handling of acetic acid and ether at approximately 220°F., where pipe and valves gave 2 years of trouble-free service, thus resulting in conversion to duplicate equipment on a second installation.

From the standpoint of corrosion resistance, there seems to be no limiting temperature on the use of high-silicon iron if the composition is closely controlled and if the castings are properly made. However, the physical properties of high-silicon iron are such as to warrant special consideration under certain operating conditions. For example, high-silicon iron pumps are handling successfully 50 to 75 per cent acetic acid at approximately 280°F. When working at this temperature range, it is desirable to provide facilities for warming the pumps before operation is started, thus eliminating quick temperature change and preventing possible damage from heat shock.

In the manufacture of acetic acid from calcium carbide or acetylene gas by synthesis of acetaldehyde and oxidation to acetic acid, actual installations include kettles for preparing the mercurous sulphate catalyst, pipe and fittings for handling the catalyst, and towers for the stage where acetaldehyde is produced. In the final step, high-silicon iron valves handle 90 per cent to glacial acetic acid at the boiling point.

Chemical Stoneware.—The corrosion resistance of chemical stoneware to acetic acid can be covered by stating that it is completely inert to all concentrations from very dilute to glacial at all temperatures at which stoneware is commonly employed and acetic acid is handled and processed. (Herstein, F. E., Chemical Stoneware, *Chem. Eng.*, Vol. 53, No. 12, p. 214, 1946.)

Stoneware has two main applications in the manufacture of acetic acid. In the fermentation process, in which ethyl alcohol is fermented to form acetic acid, stoneware vessels are used for the fermentation. These are called "vinegar generators." The main advantage claimed for the stoneware generator over the more commonly used wooden type is that there is no absorption of acetic acid into the body. This eliminates evaporation, which in some cases may be as great as 1 or 2 per cent of the entire yield. Another advantage is that, since most fermentation acetic acid, or vinegar, is used in the food industries, the inherent cleanliness of this material not only serves to keep the product pure but prevents any chemical contamination.

In the concentration of dilute acetic acid, both from the fermentation process and from the manufacture by reacting calcium acetate with sulphuric acid, stoneware and chemical porcelain are used as materials of construction for distillation columns. These columns are of the sieve type with bowl, annular shell, and down pipe all made of the ceramic materials mentioned above. They are sometimes contained in a metal armoı and sometimes self-contained. The first method is preferred, as it protects against mechanical breakage and enhances resistance to thermal shock. Stoneware interconnecting piping, fittings, cocks, and pumps are used as accessory equipment on these columns.

Besides the two manufacturing applications mentioned above, stoneware can be and is used for all handling operations such as storage, pumping, and piping. Stoneware towers are used to absorb and react acetic acid fumes, which can be handled with stoneware exhausters. Stoneware boiling kettles are used for reaction, and stoneware filters for filtrations for which nutsche-type filters are applicable.

To sum up, chemical stoneware can be used for practically all manufacturing and handling applications involving acetic acid and its derivatives. It is absolutely corrosion-resistant at all concentrations and operating temperatures, and its more widespread use has been curtailed only by its comparatively high first cost.

Rubber.—Some rubber compounds have been used commercially on a limited scale, and there is good reason to believe that they warrant consideration for more extended use in industry as linings for tanks, pipes, fittings, and valves. (True, O. S., Rubber Linings, *Chem. Eng.*, Vol. 53, No. 12, p. 216, 1946.)

As a general statement, it can be said that rubber compounds are available which will successfully handle all concentrations of acetic acid at operating temperatures up to 120°F. The factors which must be taken into account in the choice of a rubber lining for this service are concentration of the acid, operating temperatures, and allowable discoloration of the acid.

The semihard and hard rubbers are generally quite resistant to all concentrations including glacial acetic acid. These compounds are also resistant to acetic anhydride. The acid attacks all the soft rubbers, including natural, GR-M, GR-A, GR-I, and GR-S. In installations where the physical characteristics of soft rubber are required in addition to protection against acetic acid, specific soft compounds can be made from either natural rubber or GR-S which will resist low concentrations of acid at atmospheric temperatures.

All rubber compounds will impart varying degrees of color to acetic acid, and in general the higher the concentration and temperature the greater the amount of color which will be extracted. When water-white acid is to be handled, special compounds are available which in a commercial installation will not impart sufficient color to be visible to the naked eye.

Monel.—Monel has good resistance to all concentrations of unaerated acetic acid, including glacial, at room temperature. (Friend, W. Z., Nickel, Nickel Alloys, *Chem. Eng.*, Vol. 53, No. 12, p. 218, 1946.) Corrosion rates are increased by a high degree of aeration, the most active concentration being in the neighborhood of 50 per cent acid. Corrosion rates are only moderately increased by increasing temperatures as long as the acid is unaerated. However, hot aerated solutions are likely to be severely corrosive.

Nickel is also resistant to unaerated acetic acid solutions of all concentrations at room temperature. However, its corrosion rate is usually increased by aeration and by increasing temperature to a greater extent than that of Monel. Inconel is usefully resistant to dilute acid solutions under most conditions of aeration and temperature but is not resistant to strong, hot solutions such as those encountered in concentrating stills.

The use of austenitic cast-nickel-iron alloys is usually confined to unaerated acetic acid solutions at room temperature. In dilute solutions they can be used at elevated temperatures because of their copper content.

Monel is used for reactors, heating coils, piping, agitators, and other equipment in connection with esterification and acetylation reactions, particularly where small amounts of sulphuric acid are also present. It is also applied to the handling of pyroligneous liquors from wood distillation. Monel and Inconel are applied to such equipment as dyeing machines, print ager covers, and accessory parts such as rolls, shafts, and piping in connection with textile finishing processes involving acetic acid.

Carbon and Graphite.—Carbon, graphite, and certain grades of impervious carbon and graphite materials have been found satisfactory and chemically resistant by laboratory tests and commercial applications to all concentrations of acetic acid at temperatures up to the atmospheric boiling point.

Impervious graphite-base products have been used in various industrial acetic acid processes as heat-transfer and conveying equipment, such as plate and bayonet tank heaters, shell and tube evaporators and condensers, centrifugal pumps, globe valves, and pipe and fittings. (Malkin, E. S., Carbon, Graphite and Karbate, *Chem. Eng.*, Vol. 53, No. 11, p. 253, 1946.) The actual operating conditions for this equipment have not been made available by the users. However, it is known that in the case of acetic acid alone and in combinations with other chemicals the equipment has been operated without any noticeable corrosion and with complete satisfaction for several years.

Laboratory tests of Karbate materials in glacial and other concentrations of acetic acid at the atmospheric boiling points showed no discoloration of the acid and no change in physical appearance of the material.

Glass-lined Steel.—All concentrations of acetic acid at room temperature can be successfully stored in single-shell, one-piece, glass-lined steel equipment, up to and including a maximum capacity of 8,000 gal. and a maximum internal pressure range of 40 to 80 psi., depending upon steel thickness and type of heads specified. (Chormann, O. I., Glass-lined Steel, *Chem. Eng.*, Vol. 53, No. 11, p. 260, 1946.)

When jacketed glass-lined steel equipment is considered for conducting reactions involving acetic acid at elevated temperatures and pressures, some modifications with respect to types of equipment and capacities are necessary.

The standard types of glass-lined steel equipment manufactured for the chemical industry have given satisfactory performance for chlorination, esterification, and sulphonation of acetic acid.

Tantalum.—Tantalum has been found inert to acetic acid or mixtures containing acetic acid at all concentrations or temperatures at which it has been tested or used. (Hunter, F. L., Tantalum, *Chem. Eng.*, Vol. 53, No. 11, p. 264, 1946.) At low concentrations and mild temperatures, other materials are sufficiently resistant so that tantalum is recommended only for severe conditions and for heat-transfer surfaces.

Tests up to 175°C. show no attack on tantalum. Above this temperature the effect, if any, is not known. As far as tests and actual service indicate, the degree of concentration, either general or localized, has no apparent effect upon tantalum.

A tantalum condenser has been in service 6 years in the distillation of crude acetic acid from wood products under conditions where the acid quickly corroded other condenser materials which had been tried.

Tantalum heaters have been used successfully for heating crude acetic acid for distillation into pure acid. In this case, the use of tantalum in the condenser was not considered necessary.

Saran.—For siphons and short pipe lines one chemical plant employs Saran tubing. The chemical resistance appears to be good enough to permit its use in moving acetic acid. The only objection is that it becomes brittle at elevated temperatures. Saran-lined steel pipe is being used for vapors at temperatures of 70 to 80°C.

Teflon.—This material has given excellent service in a number of valve applications. Solid rings have been used as valve-stem packings in acetic acid vapor at 450°F. Indications are that the packing will last as long as the valves, with no replacement required.

Mild Steel.—Phenol-formaldehyde resins can be used as coating material for mild-steel storage tanks and piping when use of existing facilities is desired. Concentration should be maintained at 99.5 per cent or higher during storage. This resin lining is good for several years.

Neoprene.—Neoprene has been successfully used for coating an exhaust fan handling hot acetic vapors at a temperature of 200 to 300°F.

Packaging

Drums for shipping are made of steel, aluminum, or stainless steel. The last is most generally favored, with aluminum next. Glass carboys and paraffin-lined barrels are used.

For tank cars stainless steel, aluminum, and wood are favored in that order. Railroad cars lined with a baked-on protective coating of a phenolic resin are also in use for glacial acetic acid.

ACETIC ACID—ACETONE—CARBON TETRACHLORIDE

Saran-lined steel pipe is in use for handling a mixture of acetic acid, acetone, and carbon tetrachloride at room temperature. Glass-lined steel pipe is also fully resistant to this condition.

ACETIC ACID—ETHER

High-silicon irons are in use for handling acetic acid and ether at 220°F. where the pipe and valves have given several years of trouble-free service, thus resulting in conversion to duplicate equipment on a second installation. An 18-8 stainless steel with 2 to 3 per cent molybdenum is satisfactory for this service.

ACETIC ACID—FORMIC ACID

Porous carbon has been used successfully as a diffuser medium for mixtures of acetic acid, formic acid, and steam in agers in the textile industry. The pipe and fitting connections are all Karbate products. No corrosion or breakage from thermal shock has occurred in over a year of service. (Malkin, E. S., Carbon, Graphite and Karbate, *Chem. Eng.*, Vol. 53, No. 11, p. 253, 1946.)

Highly alloyed stainless steels such as Worthite and Durimet 20 valves are giving satisfactory service with crude acetic acid with some formic acid present at a temperature of 200°F. These valves are in good condition after 8 months where valves in stainless compositions of lower alloy content had failed in 3 weeks. (Staley, W. D., Durimet and Durichlor, *Chem. Eng.*, Vol. 53, No. 11, p. 256, 1946.) High-silicon iron valves used on this same service where thermal shock is no problem (temperature 200°F. but no rapid fluctuation) show practically no corrosion after many months' service.

The presence of formic acid to the extent of 2 per cent or more in boiling acetic acid solutions of 25 per cent or higher causes corrosion of 18-8 stainless steels such as Types 302, 304, and 347, owing to the strongly reducing nature of formic acid. Types 316 and 317 stainless are considerably more resistant, but even they may be attacked in some cases. Under these reducing conditions materials such as copper and Monel have shown suitable corrosion resistance and are used for such equipment as heater tubes or coils. The performance of the stainless steels sometimes can be improved by addition of oxidizing agents to the acetic acid-formic acid mixtures.

ACETIC ACID—HYDROBROMIC ACID

In a combination of acetic acid with impurities of hydrobromic acid which results in a corrosive condition decidedly more severe than one from acetic alone, graphite condensers and boilers have been found to be satisfactory. (Ford, C. E., Graphite Heat Exchangers, *Chem. Eng.*, Vol. 54, No. 1, p. 93, 1947.)

Except for tantalum, none of the familiar metals and alloys has adequate resistance. Tantalum has suitable corrosion resistance and is used to a limited extent, *e.g.*, in packing-column supports.

Hard rubber is not satisfactory. Of the many types of construction material investigated, the only others to give good satisfaction from both the resistance and the fabrication standpoints are glass, porcelain, and glass-lined steel. Consequently, these materials, to the virtual exclusion of all others, are employed in all equipment throughout the system where this particular mixture occurs.

ACETIC ACID—HYDROCHLORIC ACID

Carbon, graphite, and certain grades of Karbate materials have been found to be satisfactory with a mixture of these two chemicals which resulted in corrosive conditions decidedly more severe than from acetic acid alone. The grade of Karbate materials recommended for use depends upon the temperature conditions and the impurities present.

Glass-lined steel is unaffected by this mixture even at relatively high temperatures.

ACETIC ACID—MERCURY SALTS

Durimet plug valves are said to be giving satisfactory service with 10 per cent acetic acid and mercury salts at atmospheric temperature.

ACETIC ACID—PHENYLACETIC ACID

In one chemical plant it is necessary to vaporize glacial acetic acid containing a small amount of phenylacetic acid and to superheat it to a temperature of about 600°F. The equipment in contact with this hot, airless vapor is built of Type 316 stainless steel. There is a small amount of corrosion at the welds, but otherwise the stainless steel is satisfactorily resistant to attack.

ACETIC ACID—SULPHUR DIOXIDE

In one case the acetic acid contained 0.2 per cent SO_2. When this acid was distilled in copper vessels with copper steam coils in the bottom and with acid entering the vessel at 80 per cent, it was found that corrosion could be avoided by inserting 2 ft. of silver pipe at the cold end of the tube. The coil's life was thus greatly increased.

ACETIC ACID—SULPHURIC ACID

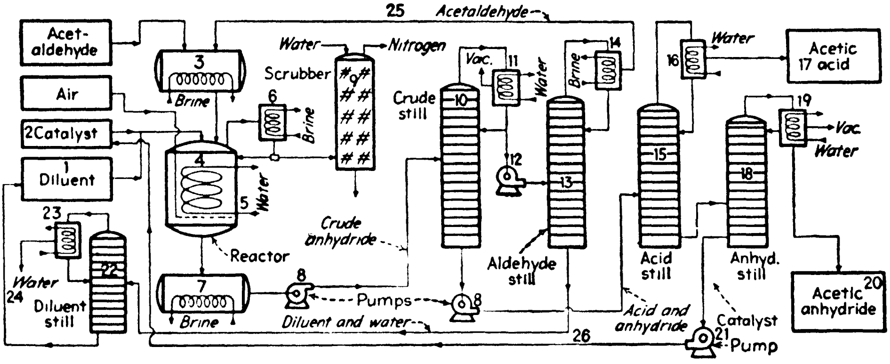
Carbon, graphite, and certain grades of impervious carbon and graphite materials, as well as glass-lined steel, have been found satisfactory and chemically resistant by commercial applications for handling a mixture of acetic acid and sulphuric acid.

Durimet pumps are said to be giving satisfactory service with a solution containing 20 per cent acetic acid and from 3 to 5 per cent sulphuric acid at room temperature. Worthite pumps and other equipment are in plant service handling a solution containing 27 per cent acetic acid and 1.5 per cent sulphuric acid.

Monel is used for reactors, heating coils, piping, agitators, and other equipment handling esterification reactions where acetic acid and sulphuric acid are present. As an example, Monel reactors and heating coils are used for production of amyl acetate from amyl alcohol and acetic acid.

ACETIC ANHYDRIDE

As with many—if not most—of the chemicals having a bad name for corrosive properties, with acetic anhydride the bad name comes from the company it keeps, *i.e.*, impurities.



Acetic anhydride from acetaldehyde.

1. Steel
2. Copper
3. Steel
4. Aluminum-lined steel
5. Aluminum
6. Type 316 or 317 stainless steel
7. Aluminum
8. Stainless steel
9. Steel
10. Stainless steel
11. Copper
12. Stainless steel, aluminum, bronze
13. Type 316 or 317 stainless steel
14. Copper
15. Copper shell and plates, aluminum bronze caps, copper reboiler
16. Copper
17. Aluminum
18. Type 316 or 317 stainless steel
19. Silver, aluminum
20. Aluminum
21. Type 316 or 317 stainless steel, high-silicon iron
22. Copper

Production

Materials of Construction.—In the so-called "chemical" processes for anhydride production, involving sodium acetate and sulphur chlorides or related materials, production is usually accomplished in cast-iron reaction vessels. Depending on the design of units, iron or steel distilling and drying equipment is used for removing the liquid from the large mass of salts remaining behind. As is usual in condenser and distilling-equipment design, copper and bronze come into use for condensers, pipe lines, etc., for handling crude anhydride and for steps in the several refining operations, although iron is also usable in most places.

The final operations and storage are usually in aluminum or glass-lined steel vessels because of the entire lack of color imparted to the finished product. Type 316 also is satisfactory.

In the many vapor-phase and pyrogenic methods for production of the anhydride, chrome and nickel steels and other alloys are used because of their resistance to the temperatures and pressures encountered, as well as their chemical stability to the reactants. Several processes involving pyrolysis are negatively catalyzed by iron and nickel, and copper or bronze tubes and parts suitably shielded from the effects of heating have been recommended. The steps of purification and refining again use copper and aluminum in the same ways as do the chemical methods. (Othmer, D. F., Acetic Anhydride, *Chem. & Met. Eng.*, Vol. 41, No. 10, p. 514, 1934.)

Vapor-phase Dehydration Process.—This process in which triethylphosphate was used as a catalyst was carried out in two steps by the Germans. (Bidlack, V. C., F. J. Curtis, and J. M. Harris, Alexander Wacker Gesellschaft für Elektrochemische Industrie, Burghausen, Germany, OPB Report 208, U.S. Department of Commerce.)

Acetic acid was fed to a vaporizer made of Type 317 stainless steel and heated with steam coils. The acid was vaporized under a pressure of about 200 mm. Hg abs. The vapors passed through the catalyst vaporizer, a horizontal, steam-jacketed 18-8 Mo stainless-steel tube, to which was fed liquid triethylphosphate.

Mixed vapors passed through a preheater and cracking furnace, which consisted of coils of Sichromal (Si-Cr-Al) tubing heated in electric-resistance or gas-fired furnaces. Gases emerged from the preheater at 600°C. and from the cracker at about 700°C. A small amount of ammonia was added at the exit from the cracker to inhibit the reversal of the ketene reaction.

The coils in the preheater and especially in the cracker became caked with a very hard carbon. They were turbined twice a year. The triethylphosphate catalyst heated in the presence of carbon formed elemental phosphorus. When this carbon was blown from the tubes, it therefore ignited spontaneously and due precautions were taken.

Hot gases from the cracking furnace were cooled in four Type 317 stainless-steel coolers, the first two of which were water cooled and the last two brine cooled.

The effluent from the coolers passed to a separator from the top of which the uncondensed ketene passed to the second part of the system. Dilute acetic acid (35 per cent) flowed from the bottom of the separator.

The entire system, including the equipment for the final distillation, was kept full of nitrogen at all times to prevent acetic acid attack on the copper and consequent discoloration of the product.

Ketene gas from the separator passed through a copper scrubber through which a mixture of anhydride 85 per cent and acetic acid 15 per cent was pumped at 30 to 40°C. Vapors passed from the top of this scrubber to the bottom of a second scrubber. Liquids flowed to the raw anhydride storage tank.

In the second scrubber, more ketene was removed from the gas by scrubbing with a mixture of 10 to 20 per cent anhydride with 80 to 90 per cent acetic acid at 20°C. The scrubbing liquor was recycled with a Type 317 stainless-steel pump. Fresh acetic acid was added to this cycle, and the scrubbing liquor for the first scrubber taken from it.

In the third scrubber the gases were scrubbed with raw anhydride at 0°C., and in the fourth scrubber with 35 per cent acetic acid at 0°C.

Stripped gases, a mixture of methane, ethylene, carbon monoxide, carbon dioxide, etc., went to a vacuum pump and were discarded. The operating pressures in the system were on a gradient between approximately 200 mm. Hg abs. at the acetic vaporizer and 80 mm. Hg abs. at the vacuum pump.

Raw anhydride could not be run to concentrations above 85 per cent without turning brown owing to the presence of unreacted ketone. It was concentrated to 95 per cent by batchwise fractionation in copper equipment. The raw anhydride contained traces of compounds formed by decomposition of the catalyst which turned brown when boiled with the anhydride. They were removed as the still residues from the final distillation, which amounted to 3 per cent on the pure anhydride.

The heating coils in the still were boiled out with caustic soda solution after every eight to ten distillations to clean off the resinous cake. Large heat-transfer surfaces in the still were desirable, as they reduced caking.

Yields were 80.5 kg. of 95 per cent anhydride per 100 kg. of 100 per cent acetic acid.

Acetic Anhydride-Acetic Acid from Aldehyde.—One of the sets of plants producing acetic acid from aldehyde is used with additions for producing a mixture of acetic acid and acetic anhydride. (Wood, W. L., Production of Acetaldehydes, Acetic Acid, Acetic Anhydride and Acetone from Acetylene at the Bunawerke, Schkopau, Final Report 25, Item 22, British Intelligence Objectives Sub-Committee, His Majesty's Stationery Office, London.)

When producing anhydride, the aldehyde feed is diluted with ethyl acetate before entering the oxidizer used alternatively for acetic acid. The two are mixed in an aluminum tank and pumped by an 18-8 stainless-steel centrifugal pump to the reactor. The catalyst also goes to the aluminum mixing tank.

Aldehyde, oxygen, and nitrogen are fed into the oxidizer. The liquid leaving the oxidizer contains 4 per cent aldehyde, the ratio of anhydride to acid being 56:44.

For the separation of anhydride and acid from aldehyde, ester, and water, a silicon-iron column is used. From the head of the column passes a vapor which on condensing in the copper coil separates into two layers. Each of these layers passes away for recovery of aldehyde and ester. From the base of the column runs a mixture of anhydride and acid containing catalyst. The base runoff flows to a pot containing a silver coil, surmounted by the silicon-iron column. The liquid from the copper condenser at the top of the column flows to an aluminum storage tank.

The catalyst mud from each pot flows to a brick-lined vessel. Some acid can be returned from the stills separating the anhydride and acid to a vessel. A suspension of catalyst in acetic acid, containing 10 per cent of mixed acetates, is returned to the aluminum feed tank to the oxidizer by means of a silicon-iron centrifugal pump.

The mixed anhydride and acid from the aluminum storage vessel flows to a packed silicon-iron column, which gives acetic acid as distillate. The acid flows to an aluminum storage tank and from there is pumped by a silicon-iron centrifugal pump to catalyst sludge dilution or away for dispatch. The heater on the column is of stainless steel (Fe; Cr, 25; Ni, 20; Si, 1), and the anhydride waste flows to a cast-iron vessel.

Anhydride is finally distilled batchwise in a column made of cast iron and surmounting a cast-iron kettle. Heating is done by means of a copper coil, the condenser being of copper and the distillate cooler of 18-8 stainless steel. Storage of finished anhydride is in aluminum vessels from which it is pumped by cast-iron pumps. The first runnings of acetic acid are passed back to the still to separate the acid and anhydride.

Handling

The pure material, even with 15 per cent acetic acid which is the standard strength, can be handled in iron without serious corrosion. Worthite and Durimet equipment are in actual plant service handling acetic anhydride solutions. Copper, too, has extensive applications in its production and handling. Monel pipe lines and pump rods are used for conveying.

Silver is not attacked during the dehydration of acetic acid to form acetic anhydride. Silver-lined vats have been successfully used in its handling. (Rogers, B. A., I. C. Schoonover, and L. Jordon, Silver: Its Properties and Industrial Uses, *Natl. Bur. Standards Circ.* C-412.)

Aluminum and glass-lined steel are in successful service for piping, storage tanks, and other equipment for acetic anhydride. Mixtures of acetic acid and the anhydride, particularly those containing more than 10 per cent of the acid, should not be handled in aluminum but can be handled in glass.

Type 316 stainless steel is being used for valves, columns, and other equipment. High-silicon iron finds its uses too.

Packaging

Acetic anhydride is shipped in aluminum or stainless-steel drums, riveted- or welded-aluminum tank cars, or glass carboys or jugs. It is shipped also in barges fitted with aluminum tanks.

ACETIC ANHYDRIDE—SULPHURIC ACID

Acetic anhydride in contact with water decomposes to form acetic acid, which corrodes iron and certain other metals. In the presence of sulphuric acid, this decomposition is violent with the evolution of heat. (Manufacturing Chemists Association, "Acetic Anhydride," Chemical Safety Data Sheet SD-15, Washington, 1947.)

ACETONE

Acetone is one of the relatively few chemicals that is without effect on any metal or other common material of construction, with the possible exception of certain plastics and other organic materials for which it is a solvent.

Production

Materials of Construction.—Ordinary cast iron and mild steel are used for much of the equipment in the production of acetone. Copper is, of course, the usual standard material for fractionating columns and condensers and is therefore widely used in acetone production.

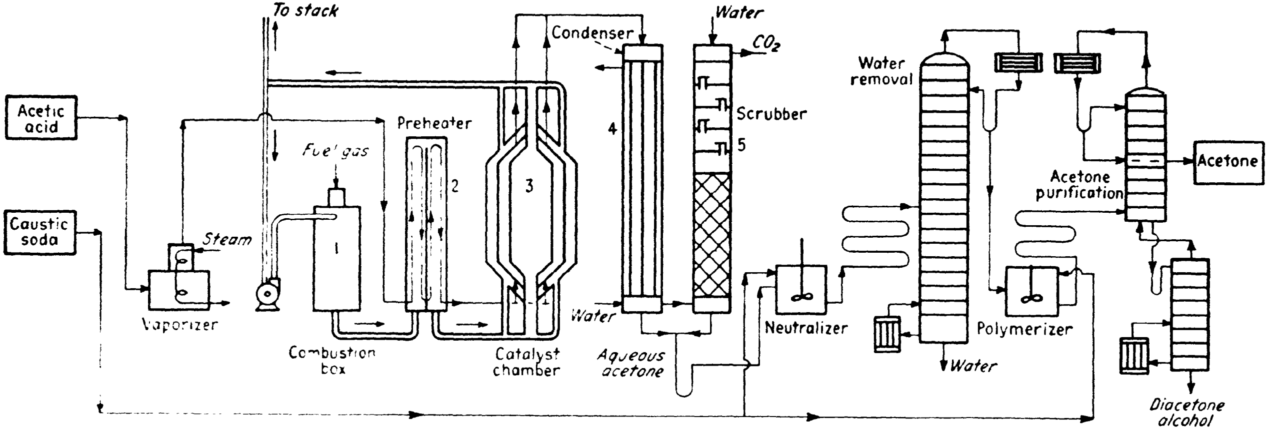
Acetic Acid Process.—Production of acetone in Germany has been reported by the British. (Wood, Lt. Col. W. L., Production of Acetaldehyde, Acetic Acid, Acetic Anhydride and Acetone from Acetylene at the Bunawerke, Schkopau, Final Report 75, Item 22, British Intelligence Objectives Sub-Committee, His Majesty's Stationery Office, London.)

Vaporizers are constructed of mild steel, lined with porcelain tiles. (If copper had been available, it was stated that this metal would have been used.) The vaporizers contain an 18-8 chrome-nickel stainless-steel coil.

The preheater consists of coils of chrome-steel (Cr, 25; Ni, 20; Si, 1; C, 0.15 max.) tubes. The coils are fed by a manifold into which acetic acid vapor passes from the vaporizer by a tube of NCT$_3$, the preheated vapors being collected in another manifold at the outlet of the preheater. The preheater tubes are housed in a mild-steel-sheet casing.

The catalyst chamber, heated by gases from the preheater, consists of cylindrical vessels with conical ends. The catalyst is composed of cerium oxide deposited on pumice. It is disposed in the inner annulus formed by several cylinders. Preheated vapors enter the annulus at the lower end, the products of decomposition leaving at the top. The temperature in the chamber is held at 420° C.

The condenser is a mild-steel multitubular vessel. The carbon dioxide leavin the bottom of the condenser passes up through the water scrubber and goes



Acetone from acetic acid (Bunawerke, Schkopau).

1. Brick-lined
2. Stainless (Cr, 25; Ni, 20; Si, 1) steel tubes in mild-steel housing
3. Mild steel
4. Mild steel
5. Mild steel
6. Mild steel lined with porcelain, with stainless-steel coil
7. Mild steel
8. Mild steel
9. Mild steel

waste from the top. The aqueous acetone passes from the base to meet the acetone from the condenser. The resultant liquid is stored in a mild-steel tank.

Caustic washers are mild steel and have a slow-speed stirrer of the same metal. A 50 per cent caustic solution is added to the first washer, and organic acids are neutralized before the aqueous acetone leaves the second washer.

The first distillation is carried out in a mild-steel column. Feed from the washers is preheated and fed to the eighth plate from the bottom. The product passes to the second caustic wash. The purpose of the second treatment is to polymerize the aldehydes, etc.

The second distillation is carried out in another mild-steel plate column. The feed passes through a vaporizer similar to that before the first still. The product is acetone. The waste is essentially diacetone alcohol.

Handling

Mild steel and ordinary cast iron are most generally used for handling acetone. It is very frequently stored in wood, although steel is just as satisfactory. It can be handled in equipment made of 99.5 per cent aluminum. Worthite and Durimet equipment are in plant use for this service. Saran-lined steel pipe is in use for conveying dilute solutions of acetone.

Karbate can handle a solution of acetone of any concentration up to boiling. A Karbate acetone condenser is in use. Tubes, channels, floating head cover, floating and stationary tube sheets are of impervious graphite. Shell and baffles are steel. (Ford, C. E., Graphite Heat Exchangers, *Chem. Eng.*, Vol. 54, No. 2, p. 134, 1947.)

Monel condensers are used to handle acetone. Inconel-clad steel tanks are used for storage of acetone in pharmaceutical manufacture.

Packaging

Acetone can be shipped in mild steel.

ACETOPHENONE

One of the British engineer teams sent to Germany after the war investigated the production of acetophenone at the Ludwigshafen plant of the I.G. Farbenindustrie. (Adams, D. A. W., and W. Baird, Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.)

Production

Materials of Construction.—Materials and equipment are as follows: cast-iron stirred vessels and lead condensers and exit pipe, lead-lined measuring vessels, stills (nonagitated) with lead condenser, lead-lined agitated cylinder as receiver, chemical-stoneware circulating pump, tile-lined florentine flasks for benzene saturated with HCl and for benzene plus crude acetophenone, homogeneously lead-lined receivers, drying towers, venuleth dryers (iron) with two iron receivers, iron rack coolers, tile-lined pressure vessel, copper still, copper receiver, iron receiver, copper condenser, lead-lined reservoir.

Process.—Acetylchloride is condensed with benzene in the presence of water-free aluminum chloride with the elimination of HCl. An agitated cast-iron vessel cooled by means of a jacket with a refrigeration system is charged with benzene, aluminum chloride is added through a funnel, and a mixture of benzene and acetylchloride is run in. The acetylchloride is siphoned into the measure vessel containing the benzene.

The free hydrochloric acid carries off some entrained benzene which is separated in a florentine flask. After all the acetylchloride has been added, the cooling water is drained off and the batch stirred. The contents are then blown by means of nitrogen into a leaded, closed, agitated cylinder with cooling coils, containing water, 30°Bé. sulphuric acid (to protect the lead), and broken-up ice; the addition is so arranged that the melt first impinges on lead plate to effect efficient distribution. With local overheating during the dilution, a resinous product is formed and the yield is consequently diminished.

When the melt is completely blown, the diluted mixture is stirred and the agitation stopped to allow the mixture to settle. The bulk of the aluminum chloride liquor is then run off through a cock in the bottom via a sight glass. The mother liquor runs through a tile-lined pressure vessel fitted with a pipe reaching to the bottom so that any benzene which collects can be recovered.

The contents of the cylinder are then pumped to a tile-lined still, and the benzene and acetophenone distilled off with open steam through three lead cooling pipes into a leaded agitated cylinder. Toward the end of the distillation cooling must not be too strong, as otherwise acetophenone crystallizes out and blocks the condenser. The distillate after thorough stirring is pumped to a lead vessel and is then separated in a florentine flask. The weak hydrochloric acid solution runs through a homogeneous lead-lined receiver to drain, and the benzene-acetophenone mixture goes to a similar receiver. It is then sucked through a drying tower filled with calcium carbonate to an iron vessel and blown from there into a venuleth. Here the benzene is distilled off at ordinary pressure and is run through another tower packed with caustic soda to a receiver in the basement to be held for another batch. When no more benzene distills, vacuum is applied and further benzene distilled into a pressure vessel. The distillate contains some acetophenone and is blown with nitrogen into the florentine flask for preparation with the following batch.

The residual crude acetophenone is dropped into an iron receiver and then blown into the copper still. Vacuum distillation follows using a steam jacket. The vacuum is applied by an injector system. The forerunnings pass through a copper condenser into an iron receiver. The distillate is diverted to the second receiver, and the remainder of the batch distilled until the distillate becomes yellow. The contents of the second receiver are blown with nitrogen into a lead-lined, heated reservoir or containers.

ACETYLTHIOPHENE

Acetylthiophene is produced by the liquid-phase acetylation of thiophene with acetic anhydride, giving acetic acid as by-product. (Kellett, J., and H. E. Rasmussen, Continuous Process for Acetylation of Thiophene, *Ind. Eng. Chem.*, Vol. 40, No. 3, pp. 384–389, 1948.)

Production

Materials of Construction.—Much of the equipment is constructed of glass linings. Of the stainless steels Types 304 and 446 are generally used. For parts of equipment Hastelloy D is found to be satisfactory.

The unit consists of a glass-lined steel charge vessel in which reactants are premixed, a positive displacement pump with Hastelloy D piston and Type 304 stainless-steel pump body with double check valves having Hastelloy D cones and Type 304 stainless seats, a preheater, a reactor, a reactor effluent cooler, and a product receiver. The receiver, a glass-lined autoclave, is used also for washing and neutralizing the product stream and subsequently as still pot for topping the unreacted thiophene. The reactor is Type 446 stainless steel. All charge and effluent lines in contact with the reaction mixture are Type 304 stainless steel.

Process.—The process consists essentially of pumping a stream of mixed thiophene and acetic anhydride through a thermostated bed of silica-alumina catalyst promoted with 30 per cent by weight of 85 per cent orthophosphoric acid.

ACROLEIN

Acrolein is being produced in the United States and during the war was made in Germany.

Production

Materials of Construction.—No corrosion problems have been encountered at any stage of the process used by Shell Chemical Corp. in the only commercial plant in the United States producing acrolein. Equipment construction is uniformly of mild steel. The pyrolysis furnace in which the diallyl ether is charged and converted to acrolein consists of a horizontal brick-lined cylindrical chamber.

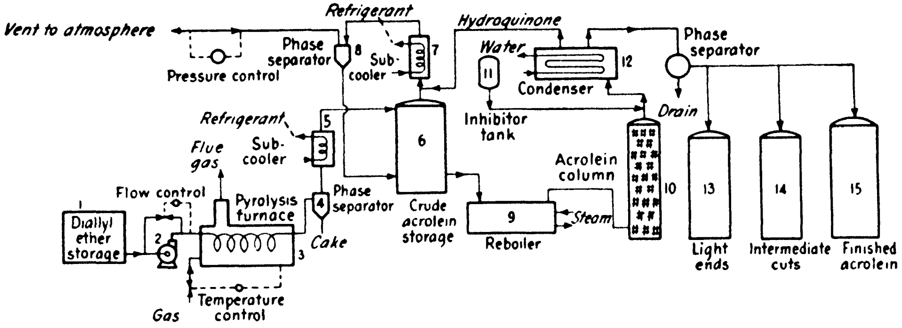
In Germany all process equipment and lines, exclusive of the catalyst tubes, were constructed of aluminum. The catalyst tubes were constructed of 18-8 stainless steel.

American Process.—The process involves the thermal cracking of diallyl ether, produced as a by-product in the production of allyl alcohol, followed by the distillation of the crude product formed to produce a refined acrolein.

Liquid diallyl ether charged to the furnace tube is vaporized and converted to acrolein, whence it passes to a cyclone separator provided for removal of the coke. It then goes to a water-cooled condenser where the major portion of the product is condensed. The stream then enters a crude storage tank, which also serves for separation of uncondensed gases and crude liquid product. These gases, containing 14 per cent acrolein by volume, then pass through a propane-refrigerated subcooler which reduces the acrolein content to 4 per cent. Liquid acrolein is returned to the crude surge drum.

Acrolein finishing is performed batchwise in a column packed with ceramic Berl saddles. The reboiler consists of a horizontal kettle with a steam coil in the lower part. There is also a shell and tube condenser.

The distillation system is charged by using the crude acrolein system pressure to effect the transfer from the crude accumulator to the batch kettle. First, propylene dissolved in the crude acrolein is removed in a "degassing" step. Acrolein condensed returns to the crude accumulator. Where liquid reflux is established, the distillation column is isolated from the crude system and is cooled.



Acrolein (cracking of diallyl ether). 1, 2, 4 to 9, 11 to 15—Mild steel. 3. Brick-lined. 10. Ceramic packing.

After degassing, a light ends fraction is removed. This cut contains the major portion of the propionaldehyde present in the crude, water, and a high concentration of acrolein. Acrolein thus recovered is returned to crude acrolein. (Watson, F. G., Shell Succeeds in Producing Acrolein, *Chem. Eng.*, Vol. 54, No. 12, pp. 106–108, 1947.) Removal of light ends is continued until a top-product acrolein is reached. Finished acrolein is directed to storage.

German Process.—The Germans made acrolein from acetaldehyde and formaldehyde over a sodium silicate catalyst at 300 to 325°C. (Anzilotti, W. F., Preparation and Reactions of Acrolein, FIAT Final Report 1157, U.S. Department of Commerce.) Degussa's acrolein unit was located in Mombach near Mainz.

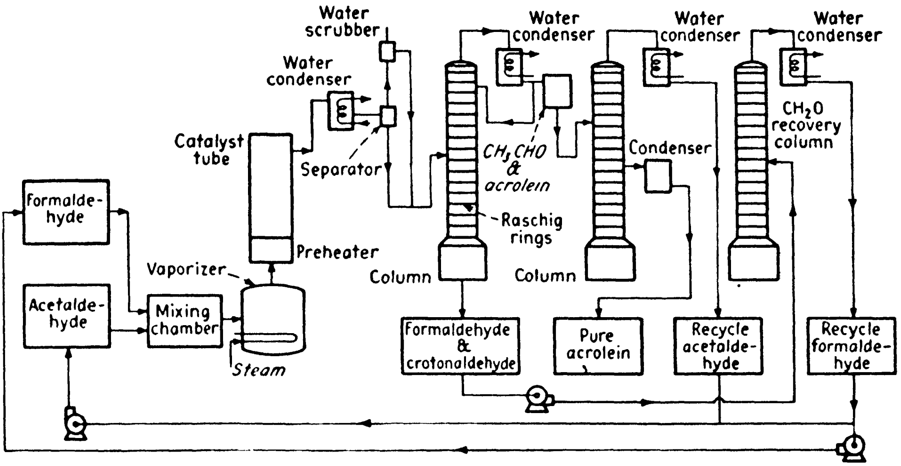
A mixture of 30 per cent formaldehyde, 30 to 34 per cent recovered formaldehyde (containing 3 to 5 per cent crotonaldehyde), and acetaldehyde (96 to 98 per cent) was fed to the vaporizer. The vaporizer was held at 110 to 120°C. The effluent gases from the catalyst bundle were condensed in a water condenser, and the condensate used as a feed for a column.

Any uncondensed aldehyde from the water condenser was scrubbed out in the water scrubber through which water was fed countercurrent. The wash water containing 0.9 to 1.2 per cent acrolein and 1.6 to 2.1 per cent acetaldehyde was fed simultaneously with the condensate into the column previously referred to.

The product drawn from the column was a mixture of 48 to 42 per cent acrolein and 42 to 48 per cent acetaldehyde which was fed partly into a second column and partly into the first column as reflux.

"Heels" from the first column contained 0.9 to 1.5 per cent crotonaldehyde and 11 to 13 per cent formaldehyde, which was used in the formaldehyde-recovery column.

Condensate from the first column (acetaldehyde and acrolein mixture) was fed into the second column. Acetaldehyde (96 to 98 per cent) was removed from the head of the column, while acrolein (97 to 98 per cent) was taken off part way up the column. Recovered acetaldehyde was used as recycle for the process, while the acrolein was used as such for chemical reaction.



Acrolein from acetaldehyde and formaldehyde. All equipment and piping are aluminum except 18-8 stainless-steel catalyst tubes.

Handling

Acrolein can be handled by ordinary steel or other common materials of construction.

Packaging

Steel cylinders are used for shipment of this material.

ACRYLONITRILE

Acrylonitrile is not a troublesome chemical to manufacture or to handle in making other materials.

Production

Materials of Construction.—At the I.G. Ludwigshafen plant the reactor was a rubber-lined steel cylindrical vessel packed with ceramic raschig rings. At the company's Leverkusen plant the catalyst vessel was rubber-lined with a ceramic-tile inner lining. The scrubbing column was cast iron. The stripper was the same size as the scrubbing column and was of a welded-steel construction. (Hasche, R. L., and J. G. McNally, Production of Acrylonitrile in the I.G. Farbenindustrie Plants at Ludwigshafen, Hüls and Leverkusen, FIAT Final Report 836, U.S. Department of Commerce.)

Process.—These three plants all used the same process. The acrylonitrile synthesis was carried out by passing a mixture of acetylene, nitrogen, and HCN through a catalyst tower where the acetylene and HCN reacted to form acrylonitrile. The gaseous reaction products were led off the top of the reactor to a countercurrent heater-scrubber, where the acrylonitrile was carried out the bottom in the water layers and unreacted acetylene was recycled from the top of the scrubber back to the reactor. The aqueous layer containing 1.5 per cent acrylonitrile was fed into the middle of a still, the water acrylonitrile azeotrope was condensed, and the two phases separated in the decanter. The product out of the top of the decanter was 80 per cent acrylonitrile.

Handling

Acrylonitrile is not corrosive to metals, not even to the ordinary ones. Therefore it can be handled in any commonly used metals or nonmetallics.

Packaging

This chemical is normally shipped in steel barrels or drums, cylinders, or tank cars.

ADIPIC ACID

Stainless steel is used for a tank in which adipic acid is dissolved in water for use in making nylon salt, hexamethylene diammonium adipate, at the Washington, W. Va., Works of E. I. du Pont de Nemours & Co. (Williams, R., Jr., How Washington Works, *Chem. Eng.*, Vol. 55, No. 9, pp. 118–121, 1948.)

In the recovery of waste nylon yarn at the Seaford, Del., plant of the same company the yarn is digested with a 50 per cent sulphuric acid solution which hydrolyzes the nylon to adipic acid and hexamethylene diammonium sulphate. The mixture is cooled, and the adipic acid crystallized out. The resultant crystalline slurry is centrifuged in a rubber-lined centrifuge to remove the crystals and returned to a lead-lined digester in which it is cooked again in order to carry the reaction closer to completion. This operation is twice repeated. Then the adipic acid is decolorized with activated charcoal, the solution filtered in a stainless-steel filter press, and the acid recrystallized in glass-lined vessels. (Lee, J. A., Nylon Production Technique Is Unique, *Chem. & Met. Eng.*, Vol. 53, No. 3, pp. 96–99, 1946.)

Chlorimet 3 pumps are used to handle this acid in crude form after purification and with slurry of crystals.

ALKANESULPHONIC ACID, MIXED

Handling

At normal temperature service glass and glass-lined equipment are resistant to the alkanesulphonic acids and are recommended for use in processing equipment. Several additional materials of construction are available. It has been found that Type 304 stainless steel and probably others are resistant to alkanesulphonic acids after special passivation, giving corrosion rates of less than 0.002 in. per year. Worthite, Durimet 20, Inconel, Stellite 6, and other high alloys have all been found to be satisfactory under some circumstances at room temperature.

In water solution, *e.g.*, 50 per cent concentration, the alkanesulphonic acids are even more corrosive. Highly alloyed stainless steels have been found very resistant to this diluted acid, and Monel moderately resistant. Polyethylene is resistant to attack and can be used at moderate temperatures, where it retains sufficient structural strength. Butyl-rubber lining compounds show considerable promise, and with some additional development work it is expected that a satisfactory butyl compound can be developed. Preliminary evidence has indicated that polyvinyl chloride-based lining compounds will be developed. For high-temperature service, glass and glass-lined equipment are recommended for the initial work. Inconel is resistant to mixed alkanesulphonic acid up to 230°F. at least, with corrosion rates of less than 0.004 in. per year.

Type 304 stainless steel has been used quite extensively in handling the acid at temperatures as high as 225°F. when traces of nitric acid are present in the reaction mixture. Actual corrosion rates have not been measured, but from the satisfactory life obtained, it is known that the rate of attack could not have exceeded 10 mils per year and probably were considerably less. Modified 18-8 stainless steels are expected to behave similarly or better.

High-alloy stainless steels such as Worthite and Durimet 20 have shown greater resistance than the 18-8 alloys at room temperature, and some of these are expected to be applicable to high-temperature service. Worthite and Stellite 6 have been used under very severe conditions in connection with pumps and have given excellent service.

Iron, steel, lead, copper, brass, bronze, and aluminum are severely attacked at both high and low temperatures.

Phosphoric acid (at high temperature) and halides of both trivalent arsenic and trivalent antimony (at lower temperatures) have been found effective inhibitors against alkanesulphonic acid corrosion under some reaction conditions. The possibility of finding effective inhibitors for most process uses seems promising.

For gaskets, Teflon is completely resistant, and in the range where structural strength is retained, polyethylene is suitable. Blue African asbestos can be used under certain conditions where surface contact is small.

Packaging

Shipments are being made in glass containers with closure gaskets composed of polyethylene. Mixed alkanesulphonic acid is being shipped in I.C.C. 1-D carboys (70 lb.) and in cases of 5-pt. bottles. It may be assumed that suitable containers are available or will be developed for shipment in drums and tank cars. (Standard Oil Co. of Indiana, *Tech. Bull.* 11, 1948.)

ALKYD RESINS

Condensation products of polyhydric alcohols and acids are known as "alkyd" and "modified alkyd resins." The most valuable of these resins are made by reacting glycerol or pentaerythritol with phthalic anhydride, maleic anhydride, and adduct compounds of maleic anhydride, obtained from a diene synthesis of the last with substances having conjugated double-bond systems. (Groggins, P. H., "Unit Processes in Organic Synthesis," 3d ed., p. 840, McGraw-Hill Book Company, Inc., New York, 1947.)

Production

Materials of Construction.—Type 304 or 347 stainless-steel resin kettles, thinning tanks, and other equipment are generally used in this country and have been reported in Germany too. (Slade, G. H., Synthetic Resins for Surface Coatings, BIOS Final Report 1794, Item 22, British Intelligence Objectives Sub-Committee, His Majesty's Stationery Office, London.) In Canada, the Canadian General Electric Co.'s plant is using for its resin kettle 20 per cent stainless-clad steel, 18-8 stabilized with columbium. This provides all the corrosion resistance of stainless steel together with ordinary carbon-steel structural features found with ordinary carbon steel. Recently pumps having hard-chrome-plated shafts have been installed. Leakage of varnish and solvents has been practically eliminated with these improved pumps. (Nelson, R. E., Modern Alkyd Resin Processing Equipment, *Can. Chem. Process Ind.*, pp. 210–213, 1947.)

Process.—In this Canadian plant, loading the charge of liquid and solid raw materials in the 18-8 Cb stainless-steel kettle is effected from weigh hoppers and scales above. Oils and glycerin are delivered by pipe lines from below-ground storage tanks. Pumps with hard-chrome-plated shafts are used. Close regulation of the kettle temperature is possible by variation in the boiler pressure and consequent changes in the temperature of the Dowtherm vapor in the jackets of the kettle.

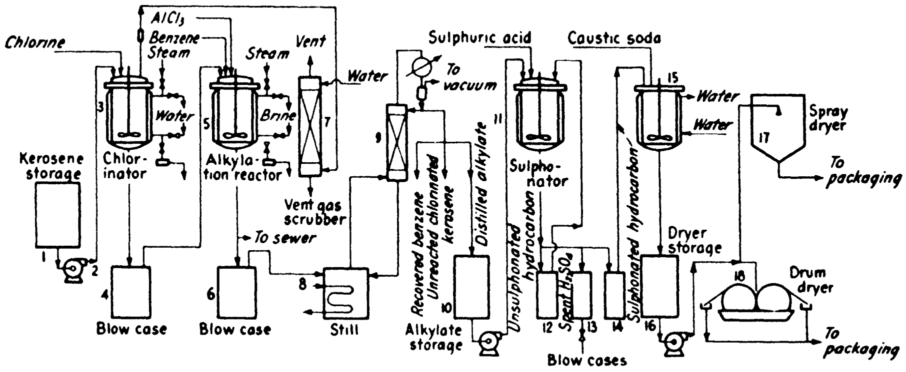
All reactions involving synthetic resins are conducted under an inert-gas atmosphere. Gas is fed to the kettle for protective atmosphere and for gas blankets or storage tanks and as operating pressure for liquid level gages on all storage tanks. The 50-psi. line is used to blow down to dry the filter cake in the Sparkler filter press.

After completion of the cooking period the kettle jackets are isolated from the Dowtherm vaporizer and the cooling cycle started. Liquid Dowtherm is forced through the kettle jackets by a pump absorbing heat from the molten resin. The partially cooled resin is then dropped by gravity into the solvent portion of the resin solution, which has been previously pumped into the stainless-steel thinning tank beneath the kettle. A reflux condenser on the vent pipe of the thinning tank is installed to prevent the escape of solvent vapors.

After blending, the hot resin is pumped to a tank room for clarification through a Sparkler-type horizontal-plate filter press. Filtered varnish is pumped to tank storage in the warehouse.

ALKYL ARYL SULPHONATES

An important group of surface-active agents are those based upon the sulphonation of aromatic hydrocarbons such as benzene and naphthalene. A class of detergents referred to as alkyl aryl sulphonates is prepared by connecting paraffin hydrocarbon groups such as a keryl or kerosene group to benzene sulphonic acid and treating the resulting material with alkali. Products of this type are manufactured in petroleum refineries as well as other plants. Benzene sulphonic acid also is prepared as an intermediate in the synthesis of phenol. Naphthalene sulphonic acids, in addition to serving as a base of wetting agents and detergents, are used for the production of naphthols to serve as dye intermediates. (International Nickel Co., Resistance of Monel and Nickel to Sulphuric Acid, *Tech. Bull.* T-3, 1948.)



Alkyl aryl sulphonates.

1. Steel
2. Steel
3. Lead-lined
4. Glass- or lead-lined
5. Glass-lined
6. Steel
7. Stoneware
8. Steel
9. Steel
10. Steel
11. Glass-lined, stainless steel
12. Steel
13. Steel
14. Stainless steel
15. Stainless steel
16. Stainless steel
17. Stainless steel
18. Steel

Production

Materials of Construction.—A considerable number of these sulphonations are made with strong sulphuric acid or with oleum at moderate temperatures. Where the sulphuric acid concentration is not allowed to fall below about 80 per cent during the reaction, steel and cast-iron reaction equipment generally is used. In some cases where 66°Bé. sulphuric acid is used and acid concentrations are likely to fall below 80 per cent, the use of Monel sulphonating equipment would be indicated as shown by test results made during sulphonation of naphthalene. These tests did not include steel or cast-iron specimens for direct comparison. However, in another test during sulphonation of phenol with 98 per cent acid at 250°F. and where the acid was diluted with water, mild steel showed a high corrosion rate. Monel, chemical lead, Hastelloys A and B, Aloyco 20, and Illium were observed to have suitable corrosion resistance under these conditions. (*Ibid.*)

Where sulphonations are carried out with strong oleums at high temperatures such as 330 to 350°F. or with weaker sulphuric acid solutions at unusually high temperatures such as 440°F., corrosion rates of all common metals and alloys are likely to be high. In these cases, sulphonators would be made of glass-lined steel.

Washing and neutralization of naphthalene sulphonic acid usually can be done in Monel equipment.

Process.—First step in the production of an alkyl aryl sulphonate is the chlorination of the kerosene fraction. Kerosene is pumped into a lead-lined, agitated, jacketed reactor. A catalyst, usually iodine, is dissolved in it. Chlorine gas is passed through the liquid. (Sittenfield, Marcus, Petroleum Chemical Detergents, *Chem. Eng.*, Vol. 55, No. 6, pp. 120–122, 1948.)

Alkylation of benzene is the next step in the production of the alkyl aryl sulphonates. Chlorinated kerosene is reacted with an excess of benzene in the presence of catalytic quantities of anhydrous aluminum chloride in a glass-lined jacketed reactor.

In both the dechlorination and the alkylation steps, hydrochloric acid can, of course, be recovered as aqueous acid. The vent gases obtained from those reactions are scrubbed in a stoneware tower with water.

The last step in the preparation of the alkyl benzene hydrocarbon is its purification. After the aluminum chloride sludge has been drawn off, the crude alkyl benzene and benzene mixture is distilled. The unreacted benzene, chlorinated kerosene, and other light-boiling constituents are removed. Finally, the alkyl benzene is distilled off and sent to the sulphonation, neutralization, and drying steps, where the dry synthetic detergent compound is produced.

The sulphonation reaction is carried out in a glass-lined jacketed reactor. The alkyl benzene hydrocarbon is mixed with sulphuric acid. The sulphonated material is drowned in a mixture of ice and water and neutralized with caustic soda. Neutralization is accomplished in a stainless-steel tank provided with cooling coils.

Handling

Considerable Monel equipment is used for the handling of alkyl aryl sulphonates in petroleum refineries and in other plants, both before and after treatment with alkalis. Inconel in either solid or clad-steel form is used for the storage and handling of some alkyl sulphate-base materials after production. The corrosiveness of these materials will depend upon whether or not free sulphur dioxide is present in appreciable amount. If it is, corrosive conditions may be severe in the vapor sections of closed storage tanks, where sulphur dioxide has an opportunity to accumulate and a sulphurous acid solution to condense. This can be prevented by using open storage tanks or removing vapors continuously from closed tanks. The nickel-chromium-molybdenum-iron alloys also are used for pumping these materials. Inconel-clad steel towers are used for the spray-drying of some sodium alkyl sulphate detergents where protection of color as well as corrosion resistance are factors.

ALKYL SULPHATES

A wide variety of detergents and wetting agents are now made by the sulphonation of fatty alcohols such as lauryl, myristyl, oleyl, palmityl, and stearyl alcohols or of fatty esters such as the monoglycerides and can be referred to generally as aliphatic or alkyl sulphates. In some cases these are converted to corresponding sodium, potassium, or ammonium salts by treatment with the corresponding alkali for use as detergents. They frequently surpass soap and sulphated oils in wetting out, emulsifying, and detergent properties. The sulphates do not hydrolyze as soaps do to give alkaline solutions.

Materials of Construction.—For these see Alkyl Aryl Sulphonates.

Where sulphonations are carried out with strong oleums at high temperatures such as 330 to 350°F. or with weaker sulphuric acid solutions at unusually high temperatures such as 440°F., corrosion rates of all common metals and alloys are likely to be high. In these cases, sulphonators probably would be made of glass-lined steel.

ALKYL VINYL ETHERS

The alkyl vinyl ethers were manufactured at Ludwigshafen by the process developed by Dr. Walter Reppe. [Boundy, R. H., and R. L. Hasche, Manufacturing of Thermoplastics in Plants of I.G. Farben., Report 1069, Combined Intelligence Objectives Committee, G-2 Division, SHAEF (Rear) APO 413, U.S. Department of Commerce.]

Production

Materials of Construction.—The reactor was constructed of iron. The carbide acetylene was handled in steel pipe lines.

Process.—The process consisted in reacting acetylene under pressure with an alcohol containing potassium hydroxide at 160 to 175°C. An iron reaction tower was two-thirds filled with catalyst solution consisting of, for example, methanol containing 20 per cent by weight of KOH. Operations will be described for production of methyl vinyl ether. A purified carbide acetylene was mixed with nitrogen to give a composition of 60 per cent C_2H_2 and 40 per cent N_2. It was compressed and introduced into the bottom of the column through a perforated steel pipe. The solution was removed continuously having a composition of 60 per cent of methyl vinyl ether and 40 per cent methanol. Dissolved acetylene was removed at 6 atm. pressure, and the methyl vinyl ether distilled at 4 atm. pressure. The remainder, containing mostly methanol, was returned to the reaction column.

ALUM

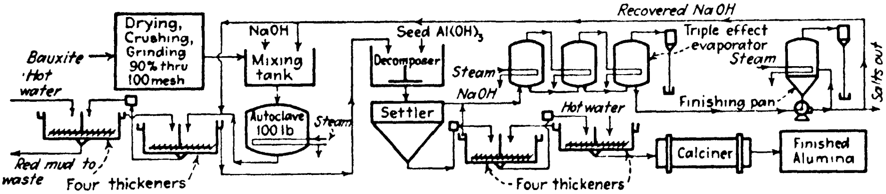
Production of alum requires one step additional to the aluminum sulphate process. Therefore, the process and materials of construction for production and handling equipment are about identical. For information of this type see Aluminum Sulphate.

ALUMINA

Alumina is used for production of aluminum by reduction in electrolytic cells. It is not corrosive, but in its manufacture special materials are used in a few pieces of equipment.

Production

Materials of Construction.—The main equipment may be ordinary cast iron or steel. But as is almost always the case, a few pieces of equipment are made of concrete such as the soda ash silos. Some plants use pressure filters covered with Monel or stainless-steel screens to hold the precoat of pulp. In the case of the alumina cooler construction, much of the feed end is stainless steel.



Alumina. Equipment is mostly ordinary cast iron and steel. Rubber belting is used for many conveyors. Soda ash is stored in concrete silos. In some plants the pressure filters are covered with Monel or stainless-steel screens to hold precoat. Much of the alumina cooler construction at feed end is stainless steel.

Process.—The principal raw materials are bauxite, lime, and soda ash. The relative amounts depend on the liquor with which they are mixed before being processed. This liquor is a solution of caustic which dissolves alumina from bauxite, forming a solution of sodium aluminate and leaving the impurities in suspension. The ingredients are mixed and pumped into digesters. On leaving the digesters, the sodium aluminate liquor with a suspension of impurities known as "red mud" passes through tanks in which it is cooled. This suspension is pumped to filter presses. The mud goes to waste after washing. Liquor filtrate and weak liquor resulting from mud washing are conveyed to coolers. They then go to precipitating tanks where aluminum trihydrate is deposited on the seed charge particles.

The contents are pumped to thickeners, where the precipitated hydrate is separated from the liquor. It is removed and washed in thickeners. The hydrate slurry flows by gravity to filters which discharge into screw conveyors feeding the rotary kilns.

The material leaves the kilns at 1800°F. and passes into a rotary cooler. On leaving the coolers the alumina falls into a conveyor which elevates it to the top of the shipping bins.

Handling

Alumina can be handled in any ordinary material.

Packaging

It is shipped in steel or wooden cars.

ALUMINUM CHLORIDE

Here is a chemical that is not too troublesome as long as it is anhydrous, but once moisture enters, trouble starts owing to the formation of hydrochloric acid.

Production

There are two important methods for the production of aluminum chloride. It can be prepared by passing dry chlorine or hydrogen chloride over heated aluminum. The other method consists of the simultaneous reduction by carbon and chlorination by gaseous chlorine of alumina-bearing materials.

Materials of Construction.—The carbonizing furnaces are silica brick, fireclay tile, and firebrick. The chlorinating furnaces are iron lined with firebrick with a layer of bauxite between iron and brick. The remainder of the equipment may be ordinary iron.

Process.—The second of these processes, *i.e.*, the reduction by carbon and chlorination by chlorine of alumina-bearing materials, is practiced by Gulf Refining Co. (McAfee, A. M., Cheap Aluminum Chloride, *Chem. & Met. Eng.*, Vol. 36, No. 7, pp. 422–424, 1929.) Crude bauxite ore is calcined in an internally heated rotary kiln at about 1800°F. to drive off free and combined moisture. From the kiln the bauxite is delivered by belt conveyor and bucket elevator to a weighing hopper, where it is added to a coking coal. The mixture is pulverized and sent to the overhead hoppers which feed into mixing vats to which is delivered a liquid binder. The mixers discharge into machines which press the bauxite, coal, and binder into briquettes.

Before chlorinating, all hydrocarbons and moisture must be driven out of the charge. Hence the briquettes are heated to 1500°F. The hot carbonized briquettes are then charged to the chlorinating furnace. The furnace shaft consists of two courses of circular firebrick, and behind these is a layer of powdered bauxite incased in an iron jacket. The object of the powdered bauxite is to protect the iron from chlorine. Near the top of the shaft are inlets for chlorine, and near the bottom an outlet for aluminum chloride leading to condensers. Briquettes are introduced and heated to the desired chlorinating temperature of

1600°F. The chlorine is turned on for 8 to 10 hr. Thus the operation proceeds in any particular furnace until the firebrick lining must be removed, about 100 days.

Handling

In general, most reactions involving the use of aluminum chloride can be carried out without danger in iron or steel equipment, provided that no free or combined moisture is present. (Anon., Aluminum Chloride, *Chem. & Met. Eng.*, Vol. 41, No. 10, p. 515, 1934.) When running intermittently, it is usually desirable to see that the equipment is flushed out after the last run with dry air or anhydrous solvent to remove the HCl. If these precautions are not observed, moisture is attracted by the deliquescent vapors with the result that the acid attacks the vent line and the sides of the reaction vessel.

The solution has an acid reaction, and to prevent contamination it should be stored and handled by acid-resistant materials. Type 304 stainless steel is being used to handle a 10 per cent solution. Type 316 is superior. Worthite equipment is in plant service handling solutions at room temperature. Durimet 20 is said to be resistant to all concentrations of aluminum chloride at moderate temperatures.

Nonmetallic materials are, of course, useful for handling this acid solution. Glass-lined kettles are in use. Soft and hard rubber can be used to handle solutions up to saturation at 150°F. Phenolic and vinyl copolymer protective coatings are said to be good.

Nickel-clad steel tanks are used for dissolving solid aluminum chloride. Monel and nickel-clad steel reactors are used in isomerization of hydrocarbons where mixtures of aluminum chloride, antimony chloride, and hydrogen chloride are used as catalysts. In Friedal-Crafts reactions where only aluminum chloride and hydrogen chloride are mixed with hydrocarbons, Hastelloy B or Hastelloy C may be required for contact with liquids while Monel or nickel can be used for reactor covers and fixtures in contact with vapors.

Packaging

Anhydrous aluminum chloride is packed in iron drums, which are eminently satisfactory as long as moisture is not allowed to come in contact with the salt. Then, of course, HCl is certain to be formed in quantities which no iron container can long endure.

Aluminum chloride solution is shipped in rubber-lined tank cars or in carboys.

ALUMINUM FLUORIDE

Aluminum fluoride for use as a flux in producing primary aluminum is made by running hydrofluoric acid of 40 to 41 per cent into storage, diluting it to 15 per cent and then pumping it into the reactor feed tank. Hydrate of alumina is dropped from a cone-bottom storage bin and conveyed to the hopper bin. Both acid and hydrate are charged batchwise into make-up tanks and agitated. The batch is dropped into crystallizing tanks before any appreciable reaction occurs.

Make-up tanks are of steel construction lined with rubber and structural carbon. In the crystallizer the reaction is completed. The slurry is heated to 200°F. and agitated. Crystallization is then completed.

The mass is dropped into an agitated slurry tank from which it is pumped into rubber-lined Dorrco continuous rotary suction filters. Up to this point all piping is rubber-lined. Washed cake drops onto a belt conveyor which feeds the calciners. These are horizontal kilns lined at the firing end with firebrick. Here the hydrate is converted into a powder containing 86 per cent or more AlF_3 and 5 per cent or less water. The product is discharged and elevated into silos.

Packaging

Aluminum fluoride is shipped in paper bags.

ALUMINUM SULPHATE

The discussion here covers aluminum sulphate and not the true alums, double sulphates of aluminum, and a monovalent metal such as ammonium.

Trouble in the production and handling of aluminum sulphate is partly due to the presence of sulphuric acid. This acid is used in making this chemical, and some free acid may be present when the solid sulphate is dissolved in water.

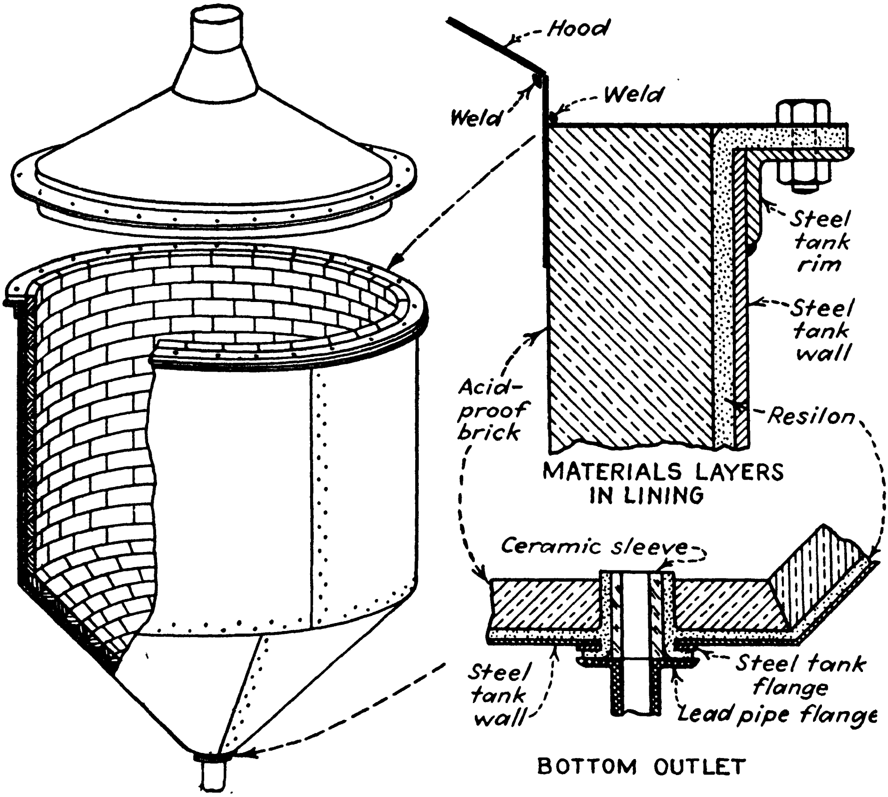
Production

Materials of Construction (Standard Process).—In the production of commercial-grade aluminum sulphate from crude bauxite, the iron content of the bauxite when converted to ferric sulphate makes the solution highly oxidizing. This combined with the boiling temperature makes the extraction or digestion process corrosive to most of the common metals except lead. (Friend, W. Z., Corrosion by Sulphate, *Chem. Eng.*, Vol. 55, No. 11, pp. 145–147, 1948.)

In fact, the manufacture of aluminum sulphate involves construction problems for which no completely adequate solution has yet been found. From the corrosion standpoint hard lead (6 per cent antimony) is very satisfactory for all strengths, but its limitations with respect to erosion and crawling are well known. In spite of these limitations hard lead continues to be used all through the process, as its first cost and the fact that it can be continually patched and repaired make it in general the most economical material for general purposes. Hard lead is mainly used for pipe lines, pumps, and valves, though the use of high-silicon iron for these purposes is increasing. (Dinsmoor, D. S., Aluminum Sulphate, *Chem. & Met. Eng.*, Vol. 41, No. 10, p. 515, 1934.)

High-silicon iron also seems to be satisfactory as far as corrosion is concerned and is used for valves and pumps. Materials satisfactory for sulphuric acid are not necessarily resistant to aluminum sulphate. For example, Pioneer alloy valves have been disappointing, while on the other hand, Pioneer shafts and impellers have done very well on pumps handling liquor and residues. Durimet has a low corrosion rate and is being compared with lead as a material for shafts and stirrers. Bronzes are attacked slowly and are used to a slight extent for fittings, particularly on weak liquors. Rubber is satisfactory within its usual limitations as to strength and temperature. (*Ibid.*) High-silicon iron pumps are extensively used for chemical equipment for handling alum solutions.

It is customary to treat the bauxite and sulphuric acid in lead-lined steel tanks. In 1946, the Montebello filtration plant of the Baltimore Bureau of Water Supply finally decided to try instead a lining consisting of an impervious membrane bonded to steel walls of the tank and faced with chemical brick. Its subsequent performance has demonstrated its superiority over the lead lining for this application. (Hopkins, E. S., Resistant Linings for Alum Boiling Tanks, *Chem. Eng.*, Vol. 55, No. 3, pp. 102–105, 1948.)



Aluminum sulphate. Best lining for boiling tank was found to be membrane bonded to tank wall faced with acidproof brick.

One of the three tanks was replaced by a butt-welded steel shell, ¼ in. thick, of the same general dimensions as the other tanks, but with a conical bottom instead of a hemispherical one. All welds were ground smooth on the inside. The new tank was welded to the supporting columns. The inside steel surface of the new tank was given a primer coat of paint containing synthetic resins. Next, sheet Resilon, ½ in. thick, was bonded by heat directly to the inside of the steel shell. This material, with a synthetic-resin base, contains magnesium silicate and a chlorinated hydrocarbon. It forms a thermoplastic membrane which is nonporous and flexible. It will not sag at 170°F. and is unaffected by abrupt temperature changes, contracting and expanding with the steel shell. Its dielectric strength is equal to that of hard rubber. The material has resistant properties comparable to those of rubber. It is suitable for use with dilute sulphuric acid and acid salts.

The membrane was faced with acidproof brick. Standard acidproof bricks, each 4½ in. thick, lined the side wall, while the same material in special shapes was used in the bottom. These bricks are dense, vitreous, and strongly resistant to acids, with but slight porosity. They are manufactured for use at temperatures not exceeding 300°F. Vitric-10, a quick-setting silicate cement, acidproof, was used to hold the bricks in place. This cement is inert to all acids except hydrofluoric, and it is a satisfactory binder at temperatures up to 750°F. Prior to use, bricks and cement were hardened by curing with a 2 per cent sulphuric acid solution for 24 hr.

To protect the bottom outlet, a ceramic sleeve was cemented to the bottom bricks and extended through the steel shell to the flanged lead pipe leading to the operating tanks.

The hood for fume removal was bolted directly to the rim of the tank with the bolts passing through the thermoplastic membrane.

A rough measurement of the tank wall temperature during the alum digestion showed an increase of only 7°F. from 86 to 93°F. Expansion of the steel is negligible, and the membrane cushion prevents fracture of the bricks. Each material layer functions as a separate entity.

The hardest service encountered is in reaction agitators, particularly in the batch process, where the cycle involves hot acid, strong-boiling aluminum sulphate solution and the erosion problems due to the necessity of keeping siliceous residues in suspension. To date the most used construction has been steel, lead-lined, with an inner lining of acidproof brick. With care in respect to detail of design this construction has fairly long life.

Agitation can be satisfactorily accomplished by eductor mixers. All parts of the eductor system are made of bronze (Cu, 28; Sn, 10; Pb, 2) except for the suction standpipe, which is lead. Bronze is used for the eductor nozzle and casing, piping, valves, and pumps; brass in the same applications suffered severe corrosion by dezincification. (Anon., Materials of Construction in Bead Catalyst Plant, *Chem. & Met. Eng.*, Vol. 53, No. 5, p. 231, 1946.)

In the production of iron-free grade aluminum sulphate from extremely low-iron-content alumina Monel can be used for digester tanks and heating coils. In the digestion of crude bauxite, corrosive conditions are considerably less severe in the cold vapor above the liquid, since ferric sulphate is not present to an appreciable extent, so that Monel is used for parts which do not enter the liquid. (Friend, W. Z., Aluminum Sulphate, *Chem. Eng.*, Vol. 55, No. 11, pp. 145–147, 1948.)

In the evaporation of commercial grades of aluminum sulphate corrosion rates due to ferric sulphate usually are too high for the economical use of Monel evaporators. In these cases lead can be used for evaporating equipment and the nickel-chromium-molybdenum-iron alloys frequently can be used for other parts. Monel is used for evaporator covers where in contact with acid vapor only. Concentrated iron-free aluminum sulphate is poured on nickel-clad-steel floor plates for cooling to prevent iron contamination.

Materials of Construction (Bureau of Mines Process).—Corrosion was the major problem encountered. The greatest difficulty lay in the distillation column and the crystallizers. After some experimentation it was realized that Type 316 or 317 stainless steel was mandatory. Weep holes in all lead-lined equipment should be specified on all equipment used at atmospheric pressures.

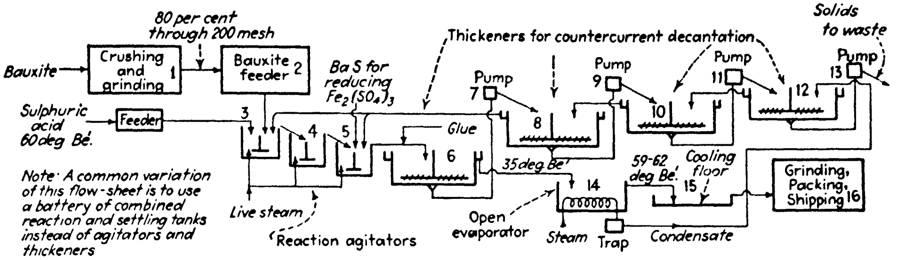
Stainless-steel or high-silicon iron pumps were used for crystal slurry, antimony lead for hot alum, and bronze for alcohol, all with satisfactory results. Lead was employed for alum, slurry, and filtrate lines, and copper for transporting all alcohol-water mixtures. (Gee, E. A., W. K. Cunningham, and R. A. Heindle, Production of Iron-free Alum, *Ind. Eng. Chem.*, Vol. 39, No. 9, pp. 1178–1188, 1947.)

Standard Process.—Aluminum sulphate usually is made by digesting finely ground bauxite or alumina with boiling sulphuric acid, frequently with air agitation during mixing. The insoluble material is allowed to settle, and the aluminum sulphate solution drawn off and sent to evaporators, where it is concentrated usually to about 57 per cent $Al_2(SO_4)_3$. The hot sirupy liquid is poured into pans where it solidifies on cooling and subsequently is crushed and ground for shipment. (Friend, *loc. cit.*)

Bureau of Mines Process.—To meet the growing demand during the war for iron-free alum the Bureau of Mines developed a process for the production of alum directly from raw materials of unrestricted supply such as low-grade bauxite. (Gee, Cunningham, and Heindle, *loc. cit.*)

The raw material for the process was crude alum, which was charged in the Type 316 or 317 stainless-steel dissolution tanks by means of chute and hopper. Alum was dissolved in water and acidified by H_2SO_4 introduced by a lead funnel. Insolubles were removed in the plate-and-frame filter press, and the clarified liquor was pumped to the evaporator, where the final adjustment of concentration was made. The alum solution was then pumped by high-silicon iron pump to the lead storage tank from which it was metered and mixed with a metered stream of alcohol in the mixing tanks at 60°C. with the immediate formation of a slurry of impure alum crystals.

By means of the coil heat exchanger the temperature was raised to the invariant point and the requisite three-phase system was attained, temperature varying from 68 to 78°C., depending upon initial conditions. Cooling and concomitant crystallization were accomplished in four successive stages of 10° differential. The cooled alum-alcohol-water mixture was collected in the slurry storage tank. Slurry was subsequently metered to the stainless-steel continuous centrifuge, where the alcoholic mother liquor was separated from alum crystals, which were then washed with fresh alcohol.



Aluminum sulphate.

1. Steel
2. Steel
3. Tanks: wood or steel with lead and brick lining. Mechanism: homogeneously lead-covered steel; high-silicon iron, Durimet, stainless steel. Covers: wood.
4. Tanks: wood or steel with lead and brick lining. Mechanism: homogeneously lead-covered steel; high-silicon iron, Durimet, stainless steel. Covers: wood.
5. Tanks: wood or steel with lead and brick lining. Mechanism: homogeneously lead-covered steel; high-silicon iron, Durimet, stainless steel. Covers: wood.
6. Tank: lead-lined wood, steel, or concrete. Mechanism: lead-covered or stainless steel. Blades: Plumbalun, Durimet, stainless steel. Covers: wood.
7. Hard lead or rubber-lined
8. Tank: lead-lined wood, steel, or concrete. Mechanism: lead-covered or stainless steel. Blades: Plumbalun, Durimet, stainless steel. Covers: wood.
9. Hard lead- or rubber-lined
10. Tank: lead-lined wood, steel, or concrete, or wood unprotected. Mechanism: lead- or rubber-covered or wood. Blades: Plumbalun or stainless steel. Covers: wood.
11. Hard lead or rubber-lined
12. Tank: lead-lined wood, steel, or concrete, or wood unprotected. Mechanism: lead, rubber-covering, or wood. Blades: Plumbalun or stainless steel. Covers: wood.
13. Hard lead or rubber-lined.
14. Lead-lined wood with hard-lead coils
15. Steel, copper, or nickel-clad steel. Solution pumps: stainless steel or high-silicon iron. Piping: lead-lined steel, lead, high-silicon iron. Valves: hard lead, stainless steel, high-silicon iron.

The alum cake was carried by screw conveyor to one of the distillation units, where adhering alcoholic liquor was distilled off. Molten alum from this operation was poured into iron pans for solidification and packaging.

Handling

In the use of aluminum sulphate the solid salt is usually dissolved in hot water to provide the desired concentration of solution. Some free sulphuric acid may be present, and the corrosiveness of the solution depends upon the concentration of ferric sulphate present. The best grades of papermaker's alum are "iron-free" with very little free acid content, and under these conditions Monel can be used for dissolving and storage tanks. However, some grades of aluminum sulphate used by paper mills may be relatively high in iron, resulting in higher corrosion rates. In most of these applications, Type 316 stainless steel is the preferred material for dissolving or storage tanks due to the possibility of some ferric sulphate being present. The nickel-chromium-molybdenum-iron alloys are used for pumps and valves.

Lead is used for handling solutions of 10 and 20 per cent sulphate. This same metal is used as a construction material for pipe lines, valves, and fittings. Highly alloyed stainless steel, such as Durimet and Worthite, for pumps is successfully used. Bronze is used for eductor mixers. Durimet 20 is resistant at all temperatures and concentrations and is used in many plants as pumps, valves, agitators, etc., for handling aluminum sulphate. One particular plant manufacturing sodium aluminum sulphate experienced corrosion on Durimet 20 presumably from the introduction of some chloride which formed dilute hydrochloric acid. High-silicon iron successfully handled this and many other alum conditions. Phenolic resin and vinyl resin coatings are used with some success. Saran-lined steel pipe is used for handling at 15 to 40°C. Glass-lined steel is unaffected at all concentrations and temperatures.

Pump packing for aqueous solutions of aluminum sulphate with or without low concentration of sulphuric acid requires African blue asbestos lubricated with graphited glyceride-free lubricant. (Lopata, S. L., Practical Approach to Packing of Chemical Pumps, *Chem. & Met. Eng.*, Vol. 51, No. 12, pp. 104–107, 1944.)

Ordinary materials can be used for pulverizing, conveying, screening, and packing equipment, as there is no corrosion problem.

Packaging

Aluminum sulphate or alum is packed in burlap or paper bags and in wooden barrels or kegs. It is also shipped in bulk in railroad cars.

ALUMINUM SULPHATE—SULPHURIC ACID

After the aluminum sulphate solution has been diluted and acidified with sulphuric acid in the acid-sulphate tank, the solution becomes extremely corrosive. The acid-sulphate tank itself is lead-lined steel, and its eductor mixer is bronze. The pipe lines carrying acid sulphate to the mixing head are lead; pumps in this line are high-alloy stainless steel, which has performed well in the service. High-silicon iron is being used in many installations involving this combination and shows excellent resistance. When originally installed, a pressure-control valve and rotameter flow-control valves were bronze throughout; in less than a year these valves were severely corroded. The plug, seat, and rod of the pressure-control valve were replaced with parts machined from Lucite (acrylic resin).

Working parts of the rotameter flow-control valves were similarly replaced by Lucite. The first rotameter bobs were stainless steel, and they corroded badly;

the present lead and bronze bobs are fairly good; high-alloy stainless steel is preferred. The old bronze valve bodies were put back in service, with the expectation of replacing them after a total service life of 2 or 3 years. The sum-total attitude toward bronze in the dilute acid-sulphate service is that it will do for parts not requiring close tolerances; Lucite has been a valuable substitute for such parts. (Anon., Materials of Construction in Bead Catalyst Plant, *Chem. & Met. Eng.*, Vol. 53, No. 5, p. 231, 1946.)

AMINO ACIDS

For the hydrolysis of gluten, which is the starting point in the production of many of the amino acids and glutamic food flavorings, several tantalum bayonet heaters and condensers were designed and fabricated for plants where soybean products are hydrolyzed to produce food flavors. Much of the other equipment in the plants is Haveg. These materials were selected because of their resistance to hydrochloric acid, which is used in the process.

Tantalum bayonet heaters are used for (1) digesting gluten in hydrochloric acid, (2) evaporating hydrochloric acid from digested gluten so that the product will not be too salty after neutralization with caustic soda, (3) condensing vapors of dilute hydrochloric acid under vacuum (26 to 28 in. Hg) during evaporation mentioned above.

Jacketed, agitated, glass-lined steel digesters are used very extensively for the acid hydrolysis of proteins.

AMMONIA

Production and handling of ammonia cause few problems of a corrosive nature.

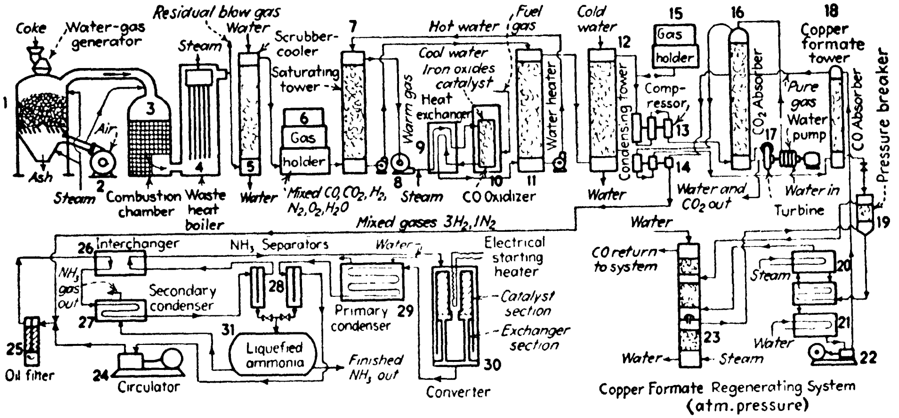
Production

Materials of Construction.—Plain carbon steel is the material most often selected for construction of equipment used in the production of ammonia. There are a few pieces of equipment, however, that call for special materials. When this is the case, stainless steels or refractories answer the purpose.

Processes.—In the ammonia synthesis from water gas by the Chemical Construction Corp.'s N.E.C. system, a modified and improved Haber-Bosch system, carbon steel is used almost throughout. In a few instances the carbon steel is protected from high temperatures by a lining of firebrick such as in the case of the water-gas generator, the combustion chamber, and the carbon monoxide oxidizer. Stainless steel is limited to the internal parts of the converter. For this purpose a low-carbon 18-8 stainless steel (either Type 304 or 347) is used.

In the case of ammonia synthesis from natural gas used in several new plants, the sulphur-free gas passes from scrubbers to a reformer furnace. It enters the top of the furnace and flows downward through tubes surrounded by hot gases as in a steam boiler economizer. These tubes are 25 per cent chromium and 20 per cent nickel steel. The outlet manifold and transfer line to the combustion chamber are made of the same composition. The combustion chamber is carbon steel with refractory lining. The converter is carbon steel with a lining of 12 per cent chromium steel. The internal parts are made of 2 per cent chromium—0.5 per cent molybdenum steel and 5 per cent chromium—0.5 per cent molybdenum steel. The other pieces of equipment are all carbon steel.

In the Claude process which operates at the high pressure of 1,000 atm., the gases pass through a number of high-alloy (Cr, 12; Ni, 60; W, 2; Fe, 25; C, 0.35) converters in series.



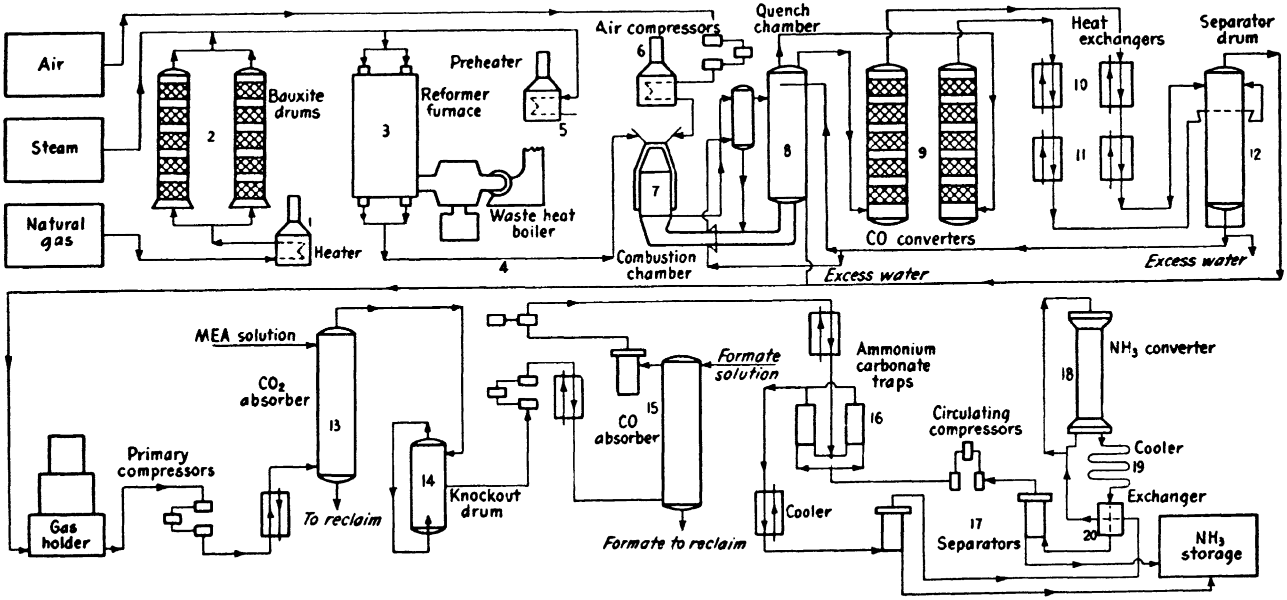
Ammonia synthesis from water gas (N.E.C. system).

1. Carbon steel, brick-lined
2. Carbon steel
3. Carbon steel, brick-lined
4–9. Carbon steel
10. Carbon steel, brick-lined
11–29. Carbon steel
30. Carbon-steel shell, stainless-steel internals
31. Carbon steel

Valves: carbon steel
Lines: carbon steel
Pumps: carbon steel

Briefly, the Casale system is characterized by the design of the converter and condenser, wherein some of the ammonia is left in the recirculated gases to temper or slow down the initial reaction in the catalyst chamber. Also, the entering gases are passed down in contact with the outside wall of the converter in order to keep its temperature below 400°C. and thus to eliminate the expensive nickel-chromium-tungsten alloy used in the Claude system. (Shreve, N. R., "The Chemical Process Industries," 1st ed., p. 402, McGraw-Hill Book Company, Inc., New York, 1945.)

The ammonia synthesis plant of Consolidated Mining and Smelting Co. at Trail, B.C., uses the process developed by Giacomo Fauser of Italy. The process employs an electrically controlled converter at 200 atm. and 500°C. and works on electrolytic hydrogen generated in a special cell. Claude liquid-air units supply the nitrogen. In this plant, gas from the sixth stage of the compressors passes through an oil separator into a common header between the compressors and thence to the precatalyst group for purification. With electrolytic hydrogen prac-



Ammonia from natural gas.

1. Carbon-steel tubes
2. Carbon-steel tubes
3. Tubes and outlet manifold, Cr, 25; Ni, 20
4. Cr, 25; Ni, 20
5. Carbon-steel tubes
6. Carbon-steel tubes
7. Carbon-steel, refractory lining
8. Carbon steel
9. Carbon steel
10. Carbon-steel shell and tubes
11. Carbon-steel shell and tubes
12. Carbon steel
13. Carbon steel
14. Carbon steel
15. Carbon steel
16. Carbon steel
17. Carbon steel
18. Carbon steel with lining of 12 Cr stainless steel, internals, Cr, 2; Mo, 0.5 and Cr, 5; Mo, 0.5
19. Carbon steel
20. Carbon steel

tically the only impurity is oxygen. The purification is effected with copper raschig rings in a nickel-steel column.

The converters or catalyst chambers are made of nickel steel. They are heated electrically during the start of operations by iron heating elements arranged in a spiral around the converter. (Kirkpatrick, S. D., Pioneering Chemical and Fertilizer Production in Western Canada, *Chem. & Met. Eng.*, Vol. 38, No. 11, pp. 626–631, 1931.)

Handling

Such equipment as cast-iron or steel reaction kettles, evaporator bodies, pumps, stills, and filter presses can be used for handling ammonia and ammoniacal solutions. One exception is a condenser where Type 304 stainless steel is used to protect against corrosion on the water side of the exchanger.

Aluminum is not seriously attacked by ammonia. A thin protective layer builds up on the aluminum surface after exposure to ammonia. This layer prevents appreciable further attack. Aluminum tubing for ammonia in refrigerating units has given good service, while aluminum storage vessels, spray equipment, and molds are widely used in contact with ammoniacal rubber latex solutions. In by-product coke plants aluminum bubble caps are used for ammonia recovery so as to avoid corrosion from the hot ammoniacal sulphide-bearing liquor. It has been reported that compressor rings of phenolic laminates are superior to cast-iron rings in ammonia equipment.

Inconel is resistant to anhydrous ammonia and ammonium hydroxide solutions under a wide range of conditions. It is commonly used for construction of ammonia desiccators to prepare nitriding atmosphere and for nitriding furnace equipment. Inconel is used for ammonia superheaters in production of certain amine compounds. Nickel and Monel are resistant to anhydrous ammonia as used for refrigeration. In aqua ammonia Monel resists solutions containing up to 3 per cent ammonia at atmospheric temperatures; the limiting concentration of ammonia for nickel is 1 per cent. "K" Monel is much more resistant than Monel and nickel to attack by stronger ammoniacal solutions. A few ammonium compounds, especially strong ammonium hydroxide, have been found to have a deleterious effect on Saran pipe. Glass-lined steel is satisfactory for storage of aqua ammonia at room temperature.

Packaging

Ammonia can be shipped in steel containers.

AMMONIA—AMMONIUM CHLORIDE

Ammonium salts when dissolved in liquid ammonia produce solutions which are actually acidic in nature. Thus, a solution containing ammonium chloride may be regarded as analogous to a solution of hydrochloric acid in water. It should be pointed out, however, that the conditions are not exactly comparable (1) because the action of such solutions upon metals is much more sluggish and

(2) because the solubilities of the products in liquid ammonia are in many cases very different from the solubilities of these same substances in water. The results of tests indicate that chrome-nickel steels and high-chromium steels are quite resistant to corrosion by solutions of ammonium chloride. It is evident that the addition of chromium to steel greatly increases the resistance to solutions of this "acid" in liquid ammonia, since various samples of iron and steel subjected to these same tests undergo appreciable attack. (Audrieth, L. F., and T. E. Franks, Corrosion of Some Alloys by Solutions of Ammonium Salts in Liquid Ammonia, *Metals & Alloys*, p. 51, February, 1938.) Nickel, wrought iron, and steel suffer appreciable corrosion by solutions of this ammonium salt. Glass-lined steel is not affected.

AMMONIA—AMMONIUM NITRATE

Ammonium salts when dissolved in liquid ammonia produce solutions which are actually acidic in nature. The results of tests indicate that chrome-nickel steels and high-chromium steels are quite resistant to corrosion by solutions of ammonium nitrate. It is evident that the addition of chromium to steel greatly increases the resistance to solutions of this "acid" in liquid ammonia, since various samples of iron and steel subjected to these same tests undergo appreciable attack. (Audrieth, L. F., and T. E. Franks, Corrosion of Some Alloys by Solutions of Ammonium Salts in Liquid Ammonia, *Metals & Alloys*, p. 51, February, 1938.)

Nickel, wrought iron, and steel suffer appreciable corrosion by solutions of this ammonium salt. Aluminum is not attacked by ammonium nitrate solution in liquid ammonia, presumably because the oxide film on the metal is not dissolved or removed.

AMMONIUM BIFLUORIDE

Among the materials that give satisfactory results with ammonium bifluoride are chemical lead, copper, Monel, and Saran. Natural rubber, carbon, and neoprene are excellent. Mild steel is very unsatisfactory. (Callaham, J. R., Fluorine Industry, *Chem. & Met. Eng.*, Vol. 52, No. 3, pp. 94–99, 1945.)

Monel is used for containers handling mixtures of ammonium bifluoride and hydrofluoric acid in the etching and frosting of glass.

AMMONIUM CHLORIDE

This chemical is made by several processes. In each case different materials of construction are required; however, little information about them has been published.

Production

Materials of Construction.—Tantalum heat exchangers have been used since 1935 for reacting chlorine with ammonia to produce chemically pure ammonium chloride. They are used to concentrate the liquor ahead of the crystallizers.

Nickel tubes and heating coils are used in evaporation of ammonium chloride. Nickel-clad steel is used for hoppers. Monel heating coils are used in ammonium chloride flux tanks.

Handling

Both cast iron and steel are frequently used in the handling of ammonium chloride. Corrosion occurs in such cases but is usually slow enough to make iron or steel the most economical selection if iron contamination can be tolerated. (Spitz, A. W., Corrosion Resistance of Steel and Cast Iron, *Chem. Eng.*, Vol. 54, No. 2, p. 135, 1947.)

Pyroflex with fused-on ceramic linings has been used for boiling concentrated solutions at 230°F. This solution was concentrated so that the water content was practically equal to the water of crystallization. Thermal shock was very severe because the tanks were emptied quickly while hot and fresh cold solution was immediately poured into the hot tank. Crystals formed immediately on cooling, introducing extremely severe forces on the brickwork and cement joints. Glass-lined steel is satisfactory.

Solutions up to 10 per cent strength can be handled in lead. Durimet 20 is highly resistant at all concentrations and temperatures. Aluminum can be used if the ammonium chloride is perfectly dry.

For solutions of medium concentration, high-silicon irons, 18-8 stainless steels, and Monel are said to be excellent while high-nickel steel and low-carbon chromium steels are fair.

AMMONIUM FLUORIDE

Some interesting experience with the corrosiveness of this chemical has been reported. (Depew, H. A., Experiences in Handling of Ammonium Fluoride Solutions, *Trans. A.I.Ch.E.*, Vol. 41, pp. 711–715, 1945.)

Handling

The room-temperature handling of ammonium fluoride solutions containing free ammonia is not difficult. They can be handled in metals, including stainless steel such as KA_2SMo; in lead; or in silicon-containing iron, as well as Karbate and some synthetics.

Steel is unsatisfactory for ammonium fluoride solutions below 20 to 25 per cent fluorine, presumably because the protective iron fluoride film will dissolve. For this purpose silver is most satisfactory, and copper-bearing metals, such as ordinary bronze or brass and aluminum bronze, do very well with or without a neoprene covering. With copper containers there is always some danger, however, from oxygen corrosion in fluoride solutions, which limits the value of this metal.

The difficulty is to choose a material resistant about neutrality (pH 6 to 8) especially when hot. For stripping columns, for example, stainless steel is not satisfactory for the acidic effluent and silver may not be satisfactory for the ammoniacal feed. One answer is Karbate, weak structurally, but chemically resistant in some grades at over 170°C.

When the temperature is not too high (95°), rubber (including neoprene) hose, rubber-lined pipes, and vessels lined with rubber are satisfactory for fluoride solutions whether slightly acidic or slightly alkaline. Also some of the plastics can be used for piping up to 85°C. Acidic ammonium fluoride does not harden rubber as HF does. Some of the newer hard-rubber synthetics have stood up remarkably well for unlagged pipe linings carrying ammonium fluoride solutions over a period of months at as high as 130°C.

Silver can be used at elevated temperatures, although it anneals slightly above the boiling point of water. If no electrolytic corrosion develops, the rate of corrosion is not sufficient to be a factor. When electrolytic corrosion develops, the rate is so great that silver is untenable.

When it is necessary to concentrate a dilute ammoniacal ammonium fluoride solution, for example, from 5 to 20 per cent F, a silver evaporator is only one of several possibilities in evaporator procedure, but it permits large capacity and large temperature range. Three of these methods to be considered are as follows:

1. An all-Karbate evaporator with a Karbate floating head and the tubes cemented in place. The catchalls can be steel, neoprene-lined, and inner-lined with a Karbate brick lining to lower the temperature of the neoprene.

2. A Karbate tube evaporator with the tubes installed in rubber-covered tube sheets and with a rubber-covered catchall. In this case, the tubes can be inserted in the tube sheets, using Flex Lock or neoprene gaskets. The limitation of this type of evaporator lies in the temperature, which must be low enough not to destroy the gaskets or the rubber tube sheets.

Although a silver evaporator is not limited by temperature or size of tube sheet, the corrosion difficulties must be considered. If the feed is an ammoniacal ammonium fluoride solution, it must not enter the silver evaporator until it has been stripped to an acidic condition. For this purpose a Karbate preheater and a Karbate bubble-plate stripper have been used. When a silver preheater is used, enough silver ions enter the solution to cause serious electrolytic corrosion in the evaporator and connecting piping.

If copper contamination in small amounts is not objectionable, it can be investigated as an alternative to silver.

In addition to these three general systems, combinations of silver and Karbate can be used.

The conclusion is that corrosion problems of silver can be overcome. For a large evaporator working at high temperatures, silver is practical. Karbate can also be used successfully.

AMMONIUM NITRATE

Corrosion must be avoided in the manufacture of ammonium nitrate in order to protect the equipment and because of the effect of the corrosion products on the finished material. Ammonium nitrate is, of course, an ingredient of explosives and has itself been involved in some unfortunate occurrences in this country and Europe.

Production

Materials of Construction.—The manufacture involves considerable handling difficulty in all stages of the process. The greatest corrosion of materials is probably in the neutralization and concentration of the ammonium nitrate solution, which contains about 50 per cent NH_4NO_3. Some metals have a very serious effect if used; others can be used with safety.

Corrosion problems have practically been eliminated by using stainless steel in place of mild steel and iron, writes a plant engineer. All pumps and most valves are of stainless-steel construction. A few all-iron globe valves are still used. These are satisfactory but require replacement or repair occasionally.

Concentration can be carried out in large pans containing agitating air and steam coils. These pans can be made of cast iron and may last several years. The steam and agitating air coils are usually Type 430 stainless steel.

Cast iron is suitable for the graining kettles, since the concentration is mainly 100 per cent NH_4NO_3. In absence of water, there is no corrosion.

High-silicon iron valves are used by some plants for handling nitrate solutions, since several years of experience have found them to be more economical than ordinary iron. One engineer reports that he has used high-silicon iron for valves and some pipe lines, but it is very brittle and he encountered expensive breakage.

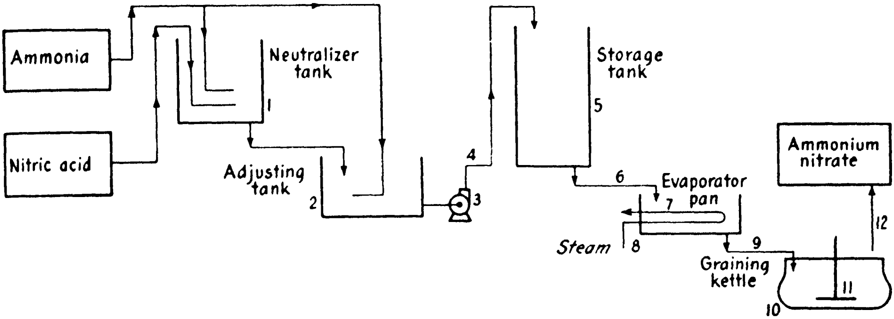
Aluminum does not render the nitrate unstable by contact with it, and the nonsparking characteristics of aluminum prevent accidental detonation. (Aluminum Co. of America, "Aluminum in the Chemical Industries," p. 7, 1944.) Solutions are evaporated and crystallized in aluminum without likelihood of attack. Other aluminum equipment in ammonium nitrate production includes condensers, evaporators, piping, screens, ammonia tanks, and piping.

It is not definitely known whether copper-corrosion products form sensitive compounds with ammonium nitrate or not, but they do lower the ignition point of such explosive mixtures as amatol. Hence copper, Monel, and the brasses and bronzes should not come into contact with the salt during any stage of its manufacture.

Tin is known to have a deleterious effect, perhaps forming a more sensitive salt, so it must be avoided. Glass-lined steel has been found by one plant to be unsatisfactory.

Process.—Ammonium nitrate is made from nitric acid and ammonia. In one plant the nitric acid is pumped continuously into a Type 430 stainless-steel neutralizing tank. Ammonia is piped into the tank to neutralize the acid to form the ammonium nitrate. The flow of ammonia is controlled by automatic pH controllers. Partially neutralized ammonium nitrate overflows into a second stainless-steel tank for final adjustment to a pH of 6.4, at which point the ammonium nitrate has an excess of 0.005 per cent NH_3. The neutralized solution is pumped by stainless-steel pumps through 3 in. o.d. Type 430 stainless-steel tubing to the aluminum storage tanks at the graining units. The solution is drained by gravity into the evaporation pan. These pans were originally glass-lined steel but were replaced with 10-gage Type 430 stainless-steel pans. The glass cracked easily and allowed the nitrate to attack the steel. The original steam and air coils were made of aluminum manufactured in 1918 and were unsatisfactory. They were replaced with Type 430 stainless-steel coils. After the material is concentrated, it is drained by gravity into cast-iron graining kettles with rotating plows. The original kettles have been in use 7 years and apparently will last another 7 years or more. It was necessary to use stainless-steel plow blades instead of steel blades because of corrosion and embrittlement.

After the ammonium nitrate is grained, it is no longer corrosive if it is kept dry. Therefore, the remainder of the cooling and treating process can be carried out in standard steel, iron, or aluminum equipment. However, owing to the hydroscopic nature of ammonium nitrate, it is necessary to keep equipment cleaned off. Otherwise, it will go into solution on damp days and begin to attack the metal equipment and concrete floors.



Ammonium nitrate.

1. Type 430 stainless steel
2. Type 430 stainless steel
3. Worthite
4. Type 430 stainless steel
5. Aluminum
6. Type 430 stainless steel
7. Type 430 stainless steel
8. Type 430 stainless steel
9. Type 430 stainless steel
10. Cast iron
11. Type 430 stainless-steel plow blades
12. Rubber

Handling

Aluminum equipment consisting of evaporators, crystallizers, pumps, and piping has been used in the production of ammonium nitrate and also for ammoniated ammonium nitrate solutions (fertilizers). These fertilizers are shipped in a fleet of aluminum tank cars.

Packaging

Ammonium nitrate is bagged in moistureproof paper bags.

AMMONIUM PHOSPHATE

There are two ammonia salts of orthophosphoric acid which are of commercial significance, chiefly as fertilizers. (Weber, W. C., Ammonium Phosphate, *Chem*

& Met. Eng., Vol. 41, No. 10, p. 517, 1934. Weber has brought the information up to date.) The "mono" salt $NH_4H_2PO_4$ has a pH of 4.4 and is extremely corrosive. Also, in its preparation from wet-process phosphoric acid the sulphuric and fluosilicic acids always present as impurities must be contended with. In the United States, the monoammonium phosphate is preferred because it is easier to produce and because of its relatively greater stability for mixing and complete fertilizers. The "di" salt $(NH_4)2HPO_4$ is of pH 8.0. It is of more balanced composition and is used in Europe but is somewhat unstable at slightly elevated temperatures or humidities. It is distinctly alkaline and not especially difficult to handle.

Production

Materials of Construction.—The accompanying tabulation gives best present practice in construction materials. The symbols following the equipment designation refer to the processes to which the unit is applicable.

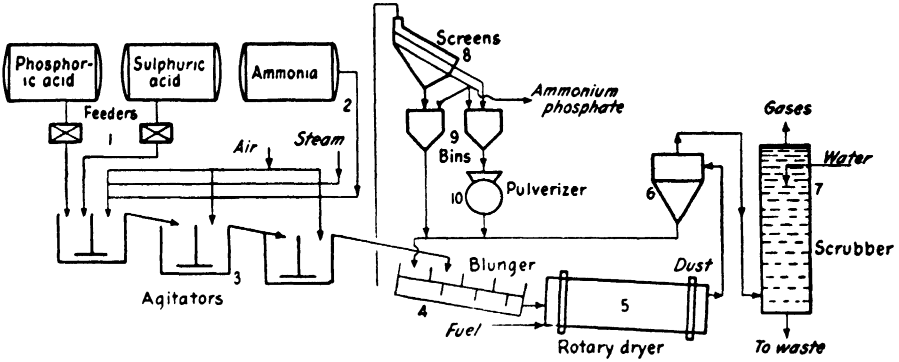
Acid feeders: (1*a*,* 1*b*) Lead-lined or rubber-covered tanks and cast-lead mechanisms
Ammonia feeding: (1*a*, 1*b*, 1*c*, 2) Cast iron and stainless steel
Saturators: (1*a*, 1*b*, 1*c*, 2) Wood or steel, lead- and brick-lined tanks, stainless-steel mechanisms, stainless distributors
Filter presses: (1*c*, 2) Cast iron or wood
Press cake dryer: (1*c*, 2) Cast-iron drums, scrapers, etc. Cast-iron and steel repulper
Evaporator: (1*c*, 2) Cast-lead, rubber-covered, or homogeneous lead-lined body; stainless or Karbate tubes
Crystallizers: (2) Iron and steel
Crystallizers: (1*c*) Stainless troughs and cast-iron or stainless stirrers
Centrifuges or salt filter: (2) Steel basket or drum, stainless screens
Centrifuges or salt filter: (1*c*) Rubber-covered or stainless
Dryer for centrifuged salt: (1*c*, 2) Steel
Blunger: (1*b*) Steel tank, steel and cast-iron mechanism
Rotary dryer: (1*a*, 1*b*) Drum, lifters, fan, cyclones, etc., all iron and steel
Screens, pulverizers, etc.: (1*a*, 1*b*) Steel and iron
Centrifugal pumps: Cast lead and Illium, all stainless, or cast iron (for di solution)
Piping: Lead, rubber-lined or iron

Process.—Methods of preparation vary somewhat. In the case of the mono salt, or Ammophos, phosphoric acid, with or without the addition of extra sulphuric acid, is neutralized with anhydrous ammonia gas in mechanically agitated saturators. The resulting slurry may be dried directly in rotary direct-

* 1. Monoammonium phosphate
  a. Saturation and direct drying
  b. Saturation and drying with fines circulation
  c. Saturation, filtration, evaporation, crystallization, and drying
2. Diammonium phosphate
  Double saturation, filtration, evaporation, crystallization, and drying

fired dryers, pulverized, and screened, or in the modification installed at Trail, B.C. (Weber, W. C., Making Phosphate Fertilizers at Trail, *Chem. & Met. Eng.*, Vol. 40, No. 2, pp. 72–75, 1933), the slurry may be blunged with previously produced and recirculated nodules and then dried, pulverized, and screened, a sized product being sent to production and the fines returned to the blunger as seed.

In the case of the di salt the phosphoric acid is customarily neutralized in two stages. In the first saturation to an $NH_3-P_2O_5$ mole ratio of 0.9 to 1.2:1, the bulk of the impurities is precipitated and removed by filter presses. The press cake is dried in a rotary drum or preferably on a twin-drum dryer.



Ammonium phosphate.

1. Lead-lined or rubber-covered tanks and cast-lead mechanisms
2. Cast iron and stainless steel
3. Wood or steel lead- and brick-lined tanks, stainless-steel mechanisms and distributors
4. Steel tank, steel and cast-iron mechanisms
5. All iron and steel drum
6. Steel
7. Steel
8. Steel
9. Steel
10. Iron and steel

Pumps: cast lead and Illium, stainless or cast iron

Piping: lead, rubber lined or iron

The substantially pure monoammonium phosphate solution is evaporated, further saturated to a mole ratio of 2:1, crystallized, centrifuged, and dried. The same type of flow sheet with elimination of the second saturation has also been used for the production of a pure (except for ammonium sulphate) and crystallized monoammonium phosphate.

A more detailed description of the mono process (*ibid.*) follows: In the manufacture of ammonium phosphate the concentrated acid flows from the storage tank to an acid feeder which delivers it in a continuous stream to the first of three series-connected, mechanical agitators. Into this first agitator 90 per cent of the ammonia is introduced in gaseous form through two stainless-steel pipes. The remaining 10 per cent of the ammonia required for neutralization and control is added in the same way to the second agitator. Cooling of the resulting slurry takes place in the third agitator. Violent boiling occurs in the first two agitators, but with neutralization to a pH of 4.5 (monoammonium phosphate), ammonia loss with the steam which is carried away by an exhaust fan should be negligible. A scrubbing tower or acid trap may be used.

The slurry formed in the reaction overflows into a heavy mixer or blunger. This consists of a pair of very heavy and rugged shafts with angular, overlapping blades, set parallel to each other in an inclined steel tank. The shafts are geared together and operate in opposite directions so that the overlapping paddles on both shafts move upward together along the center line and downward along the sides of the tank.

A large amount of dried and finished product in the form of pellets or nodules is continuously added to the blunger from an overhead bin. The blunging action effectively coats the recirculated pellets with a thin film of slurry, an ideal condition for efficient and rapid drying. The blunger discharges its product through an opening at the lower end and down a steep chute into the feed end of a rotary, direct-heat, concurrent dryer. Dryers may be fired with gas, oil, or coal using chain-grate stokers or pulverized coal. A maximum outlet temperature of 130°C. must be avoided because of the danger of decomposing the monoammonium phosphate. Discharge temperature is kept at 90 to 95°C., at which point optimum operation is obtained. The dried product drops through a grizzly and is elevated to the screens.

Gases from the dryer pass through a dust-collecting system. These collectors are extremely efficient, and dust losses are negligible. Collected solids are discharged through an automatic valve and returned to the blunger. Fan discharge goes to a scrubbing tower where all the dust and about 85 per cent of the fluorine are removed. Towers and packing are of wood impregnated with asphalt or creosote. Scrubber water is recirculated and returned to the system.

Dryer discharge is lifted to the screens by means of a bucket elevator, which is of the double-chain type with manganese-steel links and sprockets. Especially heavy construction is employed so that reliable operation may be assured even at capacities as high as 3,500 tons per day. The elevator delivers to two duplex Hummer vibrating screens. One surface is equipped with a 6- to 10-mesh screen, and the other with an 8- to 12-mesh screen. The oversize material goes to a swing-hammer mill. Pulverized material is also returned to the blunger via a second elevator. The 8- to 10-mesh material is the finished fertilizer. It is dust-free, closely sized, and well nodulized. It is carried by belt conveyor to the storage and shipping plant. This conveyor is provided with an automatic weigh hopper and continuous sampler for accurate check of the output. The fines from the screen drop into a small bin above the blunger.

AMMONIUM SULPHATE

As a general rule ammonium sulphate contains a little sulphuric acid which has not been neutralized in the process. In such a case it should be handled in lead-lined equipment. However, a neutral solution of ammonium sulphate at ordinary temperatures can be handled in carbon-steel equipment. In the case of evaporation and high temperatures one of two things may occur: Hydrolysis may take place with formation of some acid, which would give trouble, or if air is present, ferric oxide may form on the iron equipment which would be dissolved away by ammonium sulphate, and if this is repeated a sufficient number of times, of course the equipment would be corroded away. To prevent this happening there should be an excess of ammonia at all times.

Production

Materials of Construction.—Worthite pumps are used in the system of bubbling the oven gas carrying ammoniacal vapor through weak sulphuric acid. They are also used in modern plants using crystallizers and have proved successful in avoiding broken crystals. They lift the mother liquor, carrying these crystals in suspension from near the bottom of the crystallizer section and deliver this slurry to the filter-dryer unit. Worthite is not corroded by the hot weak sulphuric acid, and the rate of wear is insignificant. (Worthington Pump & Machinery Corp. *Bull.* W-350-B6.)

Graphite heaters have successfully replaced Monel coils in ammonium sulphate service. In this case slurries of the sulphate have a tendency to attack both ends of Monel coils, apparently at the cold end by successive erosion by the crystals on the protective film of the metal and subsequent corrosive attack by the solution on the base metal thus exposed. At the hot end the breakdown is caused by straight corrosion due to the higher temperature. (Ford, C. E., Graphite Heat Exchangers, *Chem. Eng.*, Vol. 54, No. 1, p. 93, 1947.)

Type 316 stainless steel is frequently used in saturators where large amounts of sulphate are present.

In one chemical plant high-silicon iron pipe is giving long service. High-silicon iron and Durimet 20 pumps and valves are widely used.

Ammonium sulphate can be processed in copper or bronze equipment such as centrifugal extractors provided there is no excess ammonia. (LaQue, F. L., *Canadian Chem. Process Ind.*, p. 185, 1938.)

Lead equipment is successfully used in the production of the sulphate by saturating coke-oven gases in sulphuric acid. The mild-steel saturator is homogeneously lead-lined.

Ammonium sulphate solutions can apparently be safely employed in contact with aluminum in many cases. However, the presence of chlorides of heavy metal salts greatly increases the action of such solutions; aluminum is resistant up to 160°F. if no free H_2SO_4 is present.

Aqueous solutions of this sulphate are being handled by all-cast-iron or stainless pumps.

Phenolic and vinyl copolymer resin coatings can be used.

Silver has been found to be unattacked by ammonium sulphate containing 5 per cent sulphuric acid. (Tupholme, C. H. S., Silver for Dyestuff Plant, *Am. Dyestuff Reptr.*, Vol. 22, p. 628.)

Good performance is to be expected from Monel in practically all parts of the production systems where acid conditions are encountered. In modern plants

Monel is being used for the construction of complete saturators and scrubbers, mother-liquor tanks, crystal settling tanks, centrifuges, vacuum filters, and accessory equipment. In continuous centrifugals, Monel has been used for baskets, discharge housings, wear plates, and fastenings. Screens of centrifugals usually are of Type 316 stainless steel, and saturators in some cases are made of this alloy.

Monel has been used for immersed saturator pumps handling the acid liquor and crystals. Such pumps are in good condition after more than 5 years' continuous service. In most systems Type 316 stainless steel is giving good performance in handling these solutions.

There has been some production of ammonium sulphate by reaction of synthetic ammonia and sulphuric acid in saturator systems. Where acid temperatures are permitted to reach rather high levels such as 200 to 230°F. owing to heat of reaction, caution should be used in the application of Monel and of the stainless steels, since the combination of such temperatures and velocity conditions is likely to cause accelerated corrosion of these materials.

Process.—Common processes for the manufacture of ammonium sulphate in by-product plants are direct systems in which gas from the coke ovens, after cooling and removal of tar, is reheated, combined with ammonia gas from the ammonia still, and delivered directly to saturators or scrubbers. In saturators, the gases are bubbled up through a layer of ammonium sulphate solution containing about 5 to 6 per cent free sulphuric acid, the temperature being maintained at about 140°F. The ammonium sulphate crystals which are formed settle to the bottom of the saturator, frequently equipped with a cone bottom, and the crystal slurry is drawn off continuously by pumping to settling tanks. The crystals are sent to centrifuges or vacuum filters for removing mother liquor, washing, and drying and are automatically discharged into sulphate storage bins. The mother liquor is heated and returned with necessary make-up acid to the saturators. Sulphuric acid concentrations in the saturators may on occasion become as high as 10 or 12 per cent.

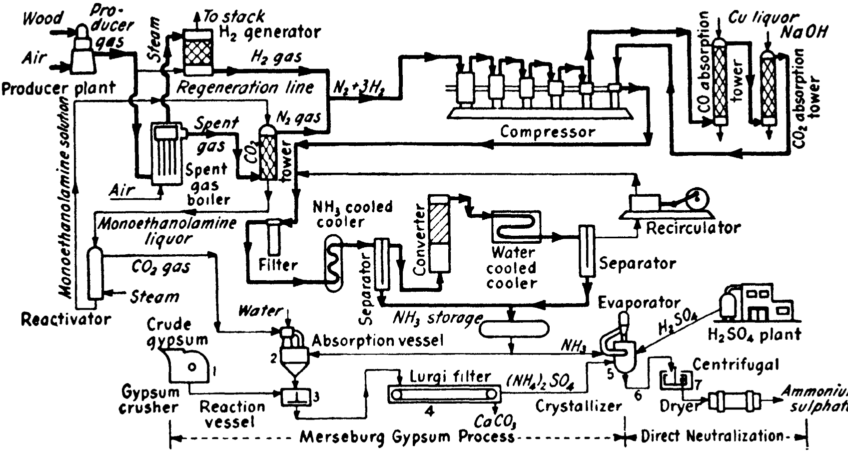
In one system the customary type of saturator is replaced with a scrubber in which the ammonia-rich gas passes upward through a packed tower countercurrently to a stream of ammonium sulphate solution containing from 4 to 10 per cent sulphuric acid, sprayed in at the top. The solution leaving the scrubber is pumped to a crystallizer from which the settled crystal slurry is pumped to a slurry tank and thence to centrifuges or vacuum filters. Temperature of the acid solution in the scrubber is normally about 122°F.

American engineers designed and put in operation in India a combination of the Merseberg reaction and direct neutralization for production of ammonium sulphate. Gypsum was crushed and cleaned to provide relatively pure calcined material. Ammonium carbonate solution was prepared in jet-type absorbers.

The pulverized gypsum and carbonate solution was fed to the first reactor, and material overflowed in series to the last unit from which reaction slurry was pumped to the belt filter. The filter cake was repulped and pumped to storage

The 40 per cent ammonium sulphate solution was pumped through a filter press to the clear-solution tank.

Rubber-lined crystallizers evaporate the sulphate solution. Circulating pumps deliver to the vacuum evaporator above with a return downcomer to the bottom of the crystallizer. Shallow stainless-steel boxes feed 30 per cent slurry to centrifuges. The sulphate is dried in a steam-heated, countercurrent rotary dryer.



Ammonium sulphate by Merseberg reaction and direct neutralization.

1. Steel
2. Wood
3. Wood
4. Rubber belt
5. Rubber-lined
6. Stainless-steel feed box
7. Stainless-steel bowl and conveyor

Pumps: rubber-lined steel
Carbonate and sulphate liquor storage: wood

Packaging

Aluminum sulphate is packaged in multiwall paper bags and is shipped in bulk in railroad cars. It is also shipped in fiber drums. The liquid is transported in steel tank trucks and tank cars.

APPLE PRODUCTS

The preparation and packing of apples and apple products require considerable processing equipment, some of which must withstand severe chemical action.

Production

Materials of Construction.—Stainless steel is used for such equipment as deaerators used to remove occluded oxygen from apple pieces. Wood, too, is used in some places. The conventional blanching of apples, for either canning or freezing, is carried out in a wooden tank.

In other plants Monel is used for apple washers in which 2 per cent hydrochloric acid is used. Monel woven-wire belts are used to convey apples through blanchers. Tanks and heating coils of the metal are used in evaporation of apple juice. Monel-lined buggies and Monel piping convey juice from presses.

Process.—In the modern plant of the C. H. Musselman Co., Biglerville, Pa., the following process is used for packing apples and apple products. The fruit is washed, graded, peeled, and inspected. It is then sliced, and the slices immersed in a 1 per cent salt brine. They are next screened and dumped onto a series of inspection belts.

If the apple pieces are subjected to a vacuum and a liquid is injected into the evacuated chamber containing the deaerated pieces, the occluded air is replaced by the liquid. For the process to be successful, the temperature and chemical characteristics of the liquid must be controlled. To do this deaeration job, the company developed special units of stainless steel.

The conventional blanching is carried out in a wooden tank filled with water and kept at a temperature close to boiling. However, Musselman has developed its own blanching technique, a continuous steam blancher. After the apple pieces have been blanched, they are ready for either canning or freezing.

APPLESAUCE

Canned applesauce is defined by the U.S. Department of Agriculture as the product made from sound, fresh apples of proper ripeness, after proper washing, peeling, coring, pulping, and processing, with or without the addition of sugar (sucrose); packed in hermetically sealed containers; and sterilized by heat.

Production

Materials of Construction.—Applesauce is very susceptible to darkening by oxidation during its preparation. Also, it should be remembered that this product is highly susceptible to metallic contamination. During manufacture, contact with iron and copper should be avoided as far as possible. For this reason, glass-lined steel, in combination with 18-8 stainless-steel fittings, is an ideal acid-resisting material for use in making this sauce. (Pheteplace, W. D., Jr., Manufacturing of Applesauce in the Digester or Pressure Cooker, *Food Ind.*, Vol. 38, No. 4, pp. 193–194, 1938.)

Choice of the material of construction for the finishing screen is of great importance. The most acceptable metals for this purpose are nickel and 18-8 stainless steel. The texture of the applesauce is governed by the diameter of perforations used for the finisher screen.

Monel is used in some plants for construction of trough-type and rotary cylindrical applesauce cookers. Cooker agitators are equipped with Monel paddles and Monel-covered shaft.

Pressure Cooker or Digester Process.—Apples from storage move along inspection belt conveyors, where undesirable fruit is removed. (*Ibid.*) Weighing and blending is done with whole unpared fruit. The apples then pass along to the paring and coring machines. Afterward they pass through a spray of water.

While apples are being fed to the glass-lined steel digester-cooker unit, a blanket of steam at low temperature is kept over the pared fruit to prevent discoloration through oxidation. Steaming or cooking is accomplished by means of injectors that feed live steam to the whole apples.

Only one moving part is used in the cooker, the combination impeller-propeller agitator of stainless steel, which has no effect upon the color or flavor of the final product.

Disintegrated cooked apples are fed through a direct connection to a paddle-type finisher of nickel or 18-8 stainless steel. The finished sauce is then put into cans.

APRICOTS

In the canning of apricots many items of equipment are made of copper or its alloys. Automatic pitters and slicers use brass and bronze castings. Copper screens are used in graders that sort the various sizes of fruit before it drops into the copper chutes that convey it to packing tables and cans. The sirup that is added at this point is handled in equipment having many copper or copper-alloy parts. (Cole, C. S., Copper, Brass and Bronze, *Food Ind.*, Vol. 7, No. 12, pp. 583–584, 1935.)

ARSENIC ACID

This chemical is not usually very corrosive in the pure state, but substantial amounts of free nitric acid in the commercial practice give much trouble. In addition, there are oxides of nitrogens resulting from the oxidation of the white arsenic which is used as raw material. The impurities in the white arsenic add considerably to the corrosion problems.

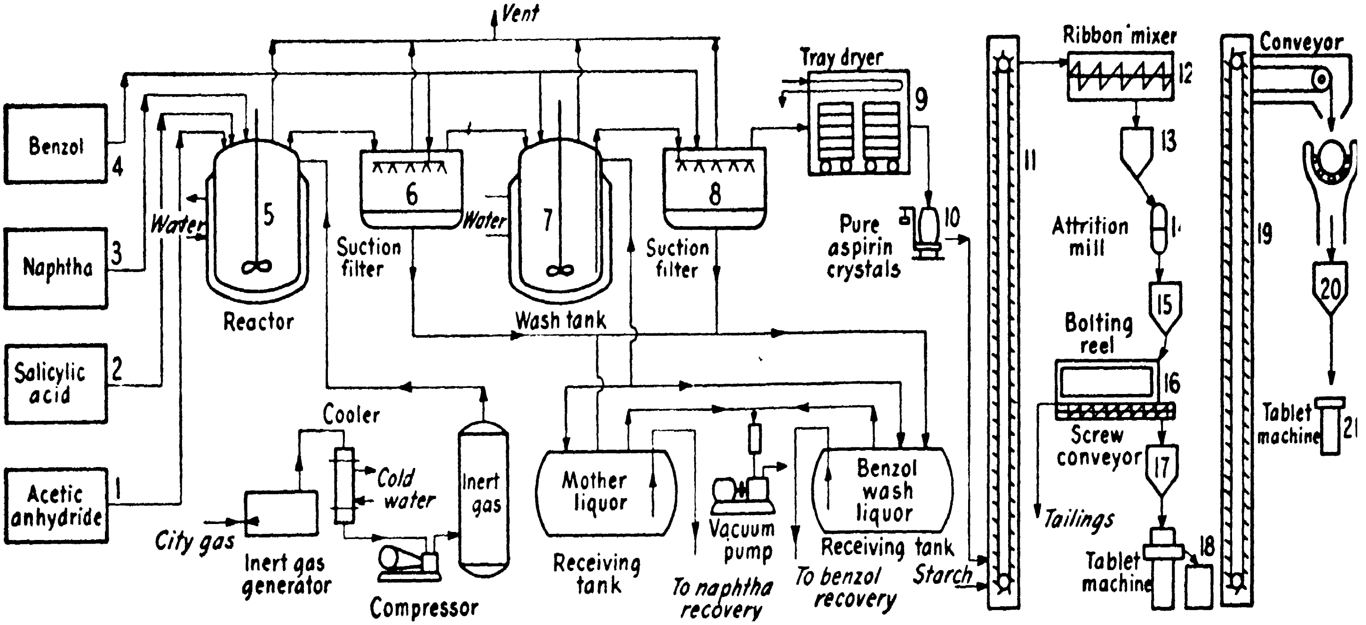
Arsenic acid has a tendency to clog pipes. In one plant steel pipe lines had to be discarded after 3½ years. Lead has been found to be much better than steel, and if the lead salt is cleaned out periodically, tubes will last 10 or 15 years.

Type 304 stainless steel is a good material for pumps, valves, and pipe lines to handle the arsenic acid, since it does not corrode or give rise to troublesome salt deposits. Worthite and Durimet equipment are in plant service handling solutions of the acid. Duriron has also been used with success.

GR-S synthetic rubber lining has given good service. Special soft rubber is satisfactory for handling any concentration up to 150°F. Karbate can be used for handling all concentrations up to boiling. Chemical stoneware and glass are also used successfully.

ASPIRIN

Aspirin is the commonly accepted name for acetylsalicylic acid. It is made by esterifying the hydroxyl group of salicylic acid. In the manufacturing process it is produced by reaction with acetic anhydride.



Aspi

1. Stainless steel
2. Wood, fiber
3. Mild steel
4. Mild steel

5. Stainless steel
6. Stainless steel
7. Stainless steel
8. Stainless steel

9. Aluminum
0. Aluminum
1-21. Stainles eel

Production

Materials of Construction.—The materials of construction throughout the new plant of one manufacturer of aspirin are predominantly stainless steel. That is, every piece of equipment that comes into contact with the aspirin product, including reactors, filters, pipes, and even the granulating equipment, is made of stainless steel in order to minimize possible contamination. Other manufacturers make extensive use of glass-lined equipment. In other plants salicylic acid is reacted with acetic anhydride in aluminum kettles and the resulting acetylsalicylic acid is crystallized in aluminum. Monel trays are used for drying aspirin powder.

Process.—Aspirin is made in the Trenton, N.J., plant of the Bayer Co. Division, Sterling Drug, Inc., by a batch process in which salicylic acid is acetylated with 98 per cent acetic anhydride. (Porter, R. W., No Headaches Here: A Modern Aspirin Plant, *Chem. Eng.*, Vol. 55, No. 3, pp. 96–98, 1948.) Salicylic acid, acetic anhydride, and naphtha, the last used as a diluent, are charged into the stainless-steel agitated reactor, and the solution brought up to acetylation temperature by hot water in the jacket. The acetylated slurry is cooled. Mother liquor is separated from aspirin crystals in a stainless-steel primary suction filter, and after several hours the crystalline mass is washed with benzol. The filters have a perforated bottom covered with a stainless-steel wire screen, burlap, and filter cloth. Crystalline aspirin is transferred to a wash tank, where it is slurred with benzol. The slurry is blown to a secondary filter, where wash liquor is drawn off and filter cake rewashed with fresh benzol.

Pure washed crystals are spread on trays and placed in an aluminum cabinet dryer. Afterward drying trays are discharged to drums, where aspirin is held until processed into tablets.

Packaging

Aspirin is packaged in glass bottles.

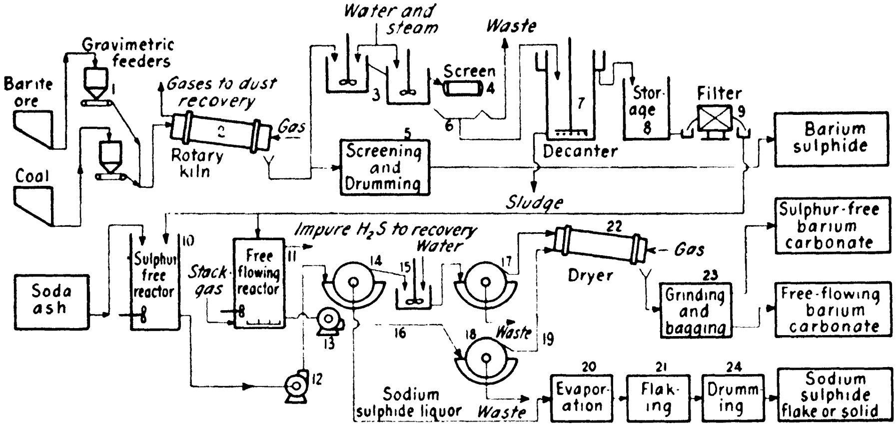
BARIUM CARBONATE

Two types of barium carbonate are manufactured, (1) "free flowing" and (2) "sulphur free." Most industries can use these two types interchangeably, except where extremely low-sulphur content is required or where a mechanical feeding device is inadequate to feed the sulphur-free material. This type packs much more easily than the free-flowing.

Production

Materials of Construction.—Free-flowing barium carbonate is made in steel equipment with the exception of pumps and pipe lines. (White, E. D., Plant That Barite Built, *Chem. Eng.*, Vol. 56, No. 1, pp. 90–93, 1949.) Corrosion is negligible in the absorbing tank, but it is so appreciable in the pumps and pipe lines that Monel equipment has been adopted. To avoid iron contamination in the sulphur-free material, all tanks are brick-lined. Pumps, pipes, and fittings are of Monel. The primary filter for sulphur-free carbonate is Monel fitted; the secondary is of steel.

Process.—Barite ore is received ground and bone-dried. Using gravimetric feeders, the ore and crushed coal are sent to the reduction kiln to produce BaS. This black ash is then fed to agitated leaching tanks and mixed with water and steam. The first two are violently agitated. The solution, with undissolved matter, then passes on through the leaching system.



Barium carbonate.

1. Steel
2. Steel
3. Brick-lined steel
4. Steel
5. Steel
6. Steel
7. Steel
8. Steel
9. Cast iron
10. Brick-lined steel
11. Steel
12. Monel
13. Monel
14. Monel
15. Steel
16. Monel
17. Steel
18. Steel
19. Monel
20. Nickel-clad steel
21. Monel
22. Steel
23. Steel
24. Steel

The first two tanks in the system are brick-lined to help combat abrasion, which is considerable; the other tanks are equipped with slow-moving agitators for decantation of the strong barium sulphide liquor from the insoluble residue. The concentrated solution is maintained at 80°C. The decanted solution goes to storage for use in production of the carbonate, while the thick slurry from the leaching system is pumped to storage for production of barium chloride.

In the manufacture of the free-flowing grade of carbonate one of the two steel absorbing tanks is charged with barium sulphide liquor from storage. This liquor passes through a conventional cast-iron plate-and-frame press. After charging, flue gas from the boilers or scrubber gas from the kiln is introduced through a series of header pipes into the base of the absorber.

Gas is pumped into the solution with a steel Nash pump until the reaction is complete. This reaction takes place in three steps:

$$BaS + CO_2 \rightarrow BaCO_3 + H_2S$$
$$BaS + H_2S \rightarrow Ba(SH)_2$$
$$Ba(SH)_2 + CO_2 + H_2O \rightarrow BaCO_3 + 2H_2S$$

The first half of the barium carbonate is precipitated with 100 per cent absorption of the CO_2. As hydrogen sulphide starts being liberated from the sulphhydrate solution, the gas-phase resistance greatly increases and absorption efficiency is lowered appreciably. During the second half of the precipitation, the hydrogen sulphide being liberated is contaminated with large quantities of nitrogen from the flue gas and small quantities of CO_2.

Carbonated slurry, which still contains sufficient alkalinity to hold oxidation products in solution, is pumped with a Monel pump to a decanting system where the liquor is sent to waste and the thickened slurry pumped to an Oliver filter. The washed cake then passes through a direct-fired dryer. It is disintegrated with a micropulverizer and sent to storage bins from which it is packed for shipment.

The sulphur-free type of carbonate is precipitated by adding soda ash in dry form to hot barium sulphide solution. Thin slurry is boiled and pumped by a Monel pump to a decanting system, where the weak sodium sulphide solution is separated and sent to storage. The slurry is then passed over a Monel-fitted rotary vacuum filter for further thickening, and a small amount of wash water is added. The filter cake, which still contains a small amount of sodium sulphide, goes to a fresh-water repulping tank and to a steel vacuum filter, where it is washed completely free from sulphides. Wash liquors go to waste, while the filter cake passes into a direct-fired dryer, then to a micropulverizer and to the packer.

Packaging

Barium carbonate is shipped in paper bags.

BARIUM CHLORIDE

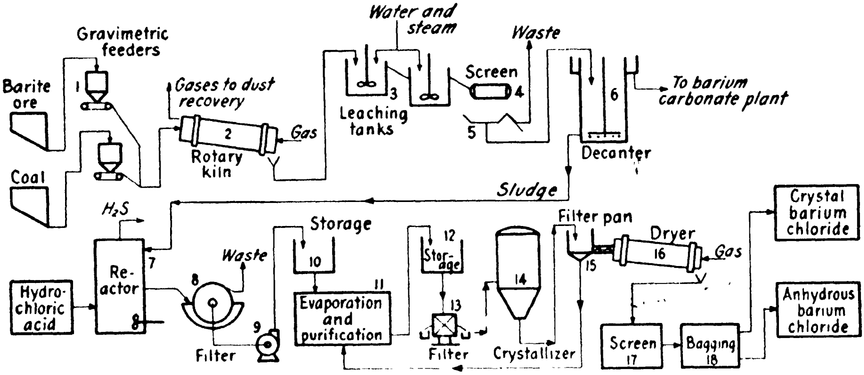
In the process that will be discussed here, considerable corrosion problems are present where barium chloride is concerned. Not that the chloride is so difficult to handle, but the trouble arises from the hydrochloric acid used in the process. (White, E. D., Plant That Barite Built, *Chem. Eng.*, Vol. 56, No. 1, pp. 90–93, 1949.)

Production

Materials of Construction.—The hydrochloric acid used calls for acidproof, brick-lined reaction tanks. All pumps, pipe linings, and fittings are either rubber-lined or constructed of Monel. All surfaces of the Oliver filter coming in contact with the liquor are of Monel. Nickel-clad steel is used for evaporator bodies in some plants. Monel is used for conveyor troughs. Inconel is used for electrodes in molten barium chloride salt at 1800°F. All tanks are brick-lined, using an acidproof cement. Wooden filter presses are also used. Glass-lined steel is fully resistant to this condition.

Process.—Barite ore is treated in a kiln with coal to form BaS. This black ash is leached with water and steam. The decanted solution goes to storage for the manufacture of barium carbonate, while the thick slurry is pumped to storage for the production of the chloride.

The slurry consists of 20°Bé. barium sulphide solution constituents from the kiln. These constituents include only a small amount of unconverted barium sulphate but considerable amounts of barium combined with iron, silica, and aluminum. These three compounds are virtually water insoluble, but they do react with hydrochloric acid to form barium chloride.



Barium chloride.

1. Steel
2. Steel
3. Brick-lined steel
4. Steel
5. Steel
6. Steel
7. Brick-lined steel
8. Monel
9. Monel or rubber lined
10. Brick-lined steel
11. Monel coil
12. Brick-lined steel
13. Wood
14. Brick-lined with Monel coil
15. Monel
16. Monel
17. Monel
18. Paper, steel

The thickened slurry is pumped to a steel tank, lined with brick and acidproof cement. Hydrochloric acid is pumped in under slight pressure by a high-silicon iron pump until a pH of 5 is reached. Barium sulphide solution is then pumped in until the pH is above 7 and all ferrous iron has been precipitated. The solution is brought to a boil and passes to a decanting system and an Oliver filter. The cake from the filter is washed free of chloride and goes to waste, and the decanted liquor and all washings go to storage.

From storage the chloride solution is pumped by a Monel or rubber-lined pump into a batch-type evaporator which is equipped with Monel steam coils. In one installation Type 304 tubes failed by cracking. The concentration is raised to 32°Bé. and contains 30 per cent $BaCl_2 \cdot 2H_2O$. At this point the solution is purified, converting all sulphur compounds to soluble barium sulphate. The hot solution is settled and sent to storage, from which it is pumped through a wooden plate-and-frame press to a batch-type vacuum crystallizer. The latter is steel with lining of brick with low-iron content and acidproof cement. Agitation is obtained with multiple side-entering agitators. The heating coil is of Monel.

More liquor is added at intervals, and evaporation is carried out under a vacuum. After sufficient concentration, the solution is cooled by means of the vacuum and the batch is pumped to a large Monel vacuum pan. Crystals are dewatered, washed free of mother liquor, and fed to a rotary Monel dryer. Moisture is reduced below 0.1 per cent.

Handling

An all-cast-iron pump is said to be in use for handling a solution of barium chloride. Durimet 20 is highly resistant at all concentrations and temperatures. Several of the stainless steels are in use for aqueous solutions, and Monel is used for various pieces of equipment. Chlorimet 2 is being used to handle solutions containing 3 per cent hydrochloric acid.

Packaging

Packaging is either in moistureproof paper bags with a sewn and waxed closure or in steel drums. The crystalline material is packed in ordinary paper bags.

BEER

Beer presents some special problems in connection with the selection of materials of construction. At certain stages of production it may be actively corrosive. At all times great care must be taken to secure and maintain the proper flavor. Also there must be no tendency to turbidity or cloudiness.

Production

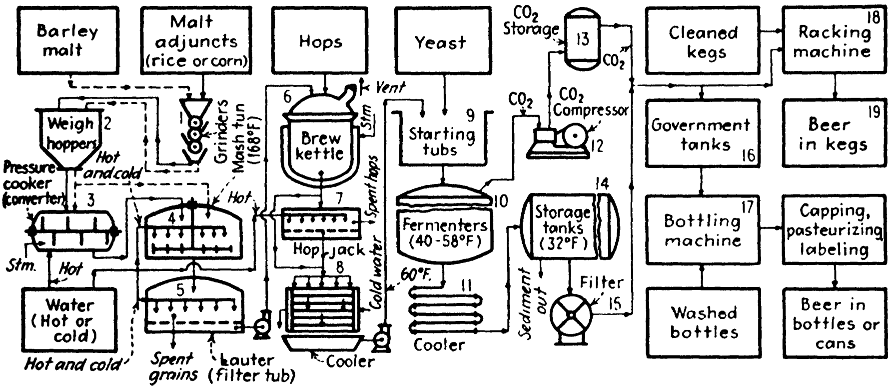
Materials of Construction.—*Copper.*—Breweries make considerable use of copper and have employed it since the earliest days of the industry. High heat conductivity and the fact that it is not corroded by beer, wort, or water are the main reasons, but ease of cleaning, ease of fabrication, and long-life economy are also important. In this industry copper is used wherever heat is being added or taken away and where the liquids are in motion.

Copper is used for brew kettles, mash tubs, coolers, filters, pipe lines, fermenting kettles, grouts, and equipment for yeast culture. Much of the interconnecting pipe is also made of copper, including coils for cooling the wort. In some cases vessels are merely lined with copper or have false bottoms made of either copper or bronze for straining purposes, as where wort is run from the mash tubs. This metal is also used for bottling and racking equipment in some breweries.

Tinned copper was used for many years in breweries, but it was shown that, as far as brewing liquors are concerned, the original bare copper is actually much better than tinned copper.

Copper has no adverse effect on taste, odor, or appearance of beer as compared with the effects produced by some other metals, but copper which has been hot-tinned or electrolytically tinned has given adverse effects.

Glass-lined Equipment.—For over 60 years the brewing industry has made use of glass-lined equipment for storage and fermentation. After fermentation in some breweries and removal of yeast, fermented beer is passed through heat-exchanger coils and sent on to the glass-lined storage tanks.



Lager beer.

1. Steel
2. Steel
3. Copper, stainless steel
4. Copper, stainless steel
5. Steel, copper, stainless steel
6. Copper, stainless steel, aluminum
7. Copper, steel
8. Copper, stainless steel
9. Steel or wood lined with pitch-type coatings
10. Glass-lined steel, wood with pitch coating, or aluminum
11. Stainless steel or copper
12. Steel
13. Steel
14. Glass-lined steel, wood lined with pitch coating, or concrete coated with mastic
15. Copper, steel, or stainless steel
16. Glass-lined
17. Stainless steel or bronze
18. Stainless steel or brass
19. Stainless steel, aluminum, or pitch-lined wood

Pumps: bronze or stainless steel
Pipes: copper

Nickel and Monel.—Nickel-clad steel is used for fermenters, combination mash and lauter tubs, cereal cookers, and hop separators. The brewing kettles are nickel-clad steel with a solid-nickel dome and vapor pipe. There is also a solid-nickel dome and vapor line on the copper kettle. The grout, collecting trough, and piping are sometimes nickel.

Monel is used for attemperator coils, CO_2 collecting tanks, bottling lines, and beer filters. The mashers may be Monel lined with Monel tubes or solid nickel. Yeast storage tanks may be made of solid Inconel.

Stainless Steel.—The introduction of the stainless steels has widened the choice of materials available for brewery equipment. Actual installations of equipment in use over periods of years have established the fact that 18-8 stainless is neutral to wort, fermenting beer, and stored beer.

Its use, therefore, for fermenters and storage vats is logical. Even yeast culture, a sensitive operation, can be successfully conducted in tanks made from 18-8. The use of stabilized 18-8 is advisable for all welded equipment. (Mitchell, W. M., Steel Alloys, *Food Ind.*, Vol. 7, No. 12, pp. 577–579, 1935.)

One of the largest breweries has used Worthite pumps for years for circulating hot, weak sulphuric acid through steel beer barrels to clean the inside coating. These pumps have proved very satisfactory for this service.

Aluminum.—This metal and its alloys are suitable materials for the fabrication of the equipment used in handling and processing malt liquors. Throughout some breweries aluminum can be found in yeast equipment, wort coolers, brew kettles, storage tanks, fermenters, filters, steam coils, pasteurizing equipment, and such miscellaneous equipment as shovels, dippers, buckets, and skimmers for lightness and freedom from corrosive attack.

At the end of the fermentation, yeast is skimmed off from the surface of the fermenting wort and removed in aluminum yeast tubs to start succeeding batches of wort fermenting and to supply yeast to the yeast plant.

Rubber.—Brewer's hose is supplied white with a sanitary cover. It is easily cleaned, and is especially developed so as not to impart taste, taint, or odor to the brew. Such rubber pipe lines and hose are used for transferring beer from one vessel to another.

Silver.—Valve disks of silver are employed for special fittings in a brewery in New Jersey, and silver pipe lines, siphons, taps, nozzles, and containers have long been used for handling and dispensing beverages in this and other plants.

Phenolic Resin.—A phenolic resin is being used in breweries for lining beer storage tanks, fermenters, filter tanks, hot wort tanks, mash and lauter tubs, pipe lines, rackers, valves, and bottle-filling equipment. The smooth resin film minimizes beer-stone accumulations on the walls of storage tanks and fermenters. The small amount of beer stone that is deposited can very easily be removed by merely scrubbing with a soft brush. Phenolic resin-lined beer storage tanks in use as long as 10 years are still giving excellent service. They are easy to clean and protect beer from iron contamination.

Packaging

Beer is put into kegs made of aluminum, wood, or stainless steel.

BENZENE HEXACHLORIDE

Production of benzene hexachloride by the photochlorination process has been described. (Neil, J., A. E. McIlhinney, and R. G. Dunlop, Manufacture of "666," *Can. Chem. Process Ind.*, Vol. 32, No. 4, p. 335, 1948.) The insecticide 666 is a mixture of at least four isomers of benzene hexachloride.

Production

Materials of Construction.—Since the production of 666 requires handling of benzene and chlorine in bulk, much thought was given to selection of equipment and materials with respect to the solvent action of benzene and the corrosive qualities of chlorine.

Glass and glass-lined steel were found to be the most satisfactory materials for the construction of most of the equipment. However, Durichlor, lead, and one or two other materials are also useful.

Process.—A glass-lined steel reaction kettle is used with chemical lead pipe with burned connections. The benzene, fed by gravity from an elevated tank, and the chlorine from a cylinder mounted on a scale are conducted separately into the kettle. A rotameter is included in the chlorine input lead to facilitate control of the chlorine flow rate.

A high-pressure quartz mercury-vapor lamp, rated at 1,000 watts, is used to irradiate the reaction mixture. The lamp is water-cooled, a quartz jacket rather than glass being used to prevent blocking off of the output in the shorter wavelength region. The kettle is vented to the atmosphere via the exhaust system.

Irradiation is accomplished outside the kettle by using a Durichlor pump to circulate the reaction mixture from the bottom via lead pipe through an external Pyrex-glass reaction cylinder and thence back through an aperture in the cover of the kettle.

The reaction cylinder with the mercury-vapor lamp mounted above it is enclosed in a cylindrical sheet-metal shield which, as a reflector, minimizes radiation losses and protects personnel from excessive exposure to this radiation. A blower system is installed to disperse ozone generated by the lamp, to prevent moisture condensation, and to serve as a cooling agent.

A bleeder valve is located near the output end of the cylinder for manual control of the output to the collecting vessel. A hood mounted over the output eliminates chlorine and benzene vapor. The output from the reactor is transferred to a glass-lined jacketed still equipped with a steam injector, where unreacted benzene and chlorine are removed by steam distillation.

The chlorine-benzene mixture proved to be extremely difficult to confine. Blue asbestos sheet rendered satisfactory service as gasket material against the corrosive and disintegrating properties of this liquid for the cover of the kettle and the still and for the apertures therein. In addition, an acid-resistant sheet packing was used in a compression seal at the ends of the Pyrex reactor tube, as well as for the flange connections at the centrifugal pump, but more frequent replacement was required at these points, however.

Chemical lead pipe was used in which to circulate the reaction mixture. It is acknowledged, however, that Pyrex glass or glass-lined steel would have provided superior corrosion resistance had it been immediately available.

In some plants aluminum hoppers equipped with screw conveyors handle benzene hexachloride.

Packaging

This chemical is shipped in fiber drums.

BENZOIC ACID

Benzoic acid gives considerable trouble when anhydrous or aqueous both in handling and production. To avoid corrosion special metals and alloys are required.

Production

Materials of Construction.—When this acid is produced by a process in which sulphuric acid is used, materials resistant to that acid are called for. Other materials are demanded when hydrochloric acid is a raw material.

Processes.—Benzoic acid is manufactured from toluene by oxidation with concentrated sulphuric acid and manganese dioxide. (Desha, L. J., "Organic Chemistry," 1st ed., p. 240, McGraw-Hill Book Company, Inc., New York, 1936.) It is also manufactured from toluene by chlorinating to benzotrichloride and hydrolyzing the latter by boiling with water and powdered iron. (*Ibid.*) With manganese dioxide, the principal product is benzaldehyde; for high yields of benzoic acid, a stronger oxidizing agent such as chromic acid is required. (Groggins, P. H., "Unit Processes in Organic Synthesis," 3d ed., p. 445, McGraw-Hill Book Company, Inc., New York, 1947.) Considerable benzoic acid is manufactured by the decarboxylation of phthalic acid, a process that yields a chlorine-free product.

Handling

Aluminum is often used for handling and processing benzoic acid, especially for anhydrous acid. It is particularly popular with German engineers. Nickel can be used also for anhydrous benzoic acid.

Such stainless steels as 18-8, Durimet, and Worthite are reported to be in service handling the acid. It is stated that it can be used satisfactorily in copper equipment.

BENZOTRIFLUORIDES

Benzotrifluoride has three synonyms: trifluoromethylbenzene, phenylfluoroform, and α-trifluorotoluene. The replacement of fluorine of the three hydrogens of the methyl group on toluene produces some interesting results.

Production

Materials of Construction.—This synthesis can be carried out in plain iron or steel equipment.

Process.—Benzotrifluoride can be prepared from benzotrichloride by the Swarts reaction in the absence of a catalyst. Commercially, anhydrous hydrofluoric acid is used in place of antimony trifluoride. The reaction takes place in an autoclave under heat and pressure, resulting in an almost quantitative yield. (Finger, G. C., Fluorine Compounds in Organic Syntheses, *Chem. & Met. Eng.*, Vol. 51, No. 6, pp. 101–103, 1944.)

Handling

Generally speaking, ordinary steel or cast iron can be used for handling, for these materials are quite stable and noncorrosive.

Packaging

Plain steel containers can be used for shipping benzotrifluorides.

BENZYLPHENOL

A lead- or glass-lined vessel fitted with an HCl absorption system is charged below 40°C. (water cooling) with phenol, benzyl chloride, and zinc chloride as catalyst. It is stirred until reaction is complete as judged by absence of smell of benzylchloride and by complete solubility in dilute caustic soda solution. The usual time required is 6 hr.

It is heated to 80°C., a little soda solution is added to neutralize, and the mixture blown to an 18-8 stainless-steel vessel fitted with 65-atm. steam for heating. There is no column for fractionation. Vacuum is applied (15 mm. pressure), and the product distilled: first fraction is mainly water, second fraction is dry phenol, third fraction (intermediate fraction) is phenol and benzylphenol, fourth fraction is benzylphenol, fifth fraction is tail runnings. The final temperature is 220°C. (Adams, D. A. W., and W. Baird, PB 80401, Office of Technical Services, U.S. Department of Commerce.)

BENZYLSULPHANILIC ACID

Production

Materials of Construction.—Two condensation vessels, cast-iron and glass-lined, with a cooling and heating jacket, and anchor-type stirrer; one measuring vessel, lead-lined for benzyl chloride; and one centrifuge are required.

Process.—One of the condensation vessels is charged with sulphanilic acid sodium salt in the form of 19 per cent acid-free solution. The solution is warmed, and sodium carbonate added. The mixture is heated to 95°C., kept at that temperature for 4 to 5 hr., and then cooled to 70°C. At this temperature 98 per cent H_2SO_4 is run in until acid to congo red. It is cooled to 20°C., and the precipitated benzylsulphanilic acid centrifuged. (Adams, D. A. W., and W. Baird, Some Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.)

BERYLLIUM SULPHATE—SAND—SULPHURIC

Over 5 years' service has been given by a high-silicon iron pump and valves handling a slurry consisting of sand, beryllium sulphate, and sulphuric acid near the boiling point. The mixture is difficult to handle because of its abrasive nature and high temperature.

BLEACHING POWDER

Formerly, bleaching powder was made on a large scale by spreading a thin layer of dry slaked lime on the floor of large concrete chambers. (Prichard,

D. A., and G. E. Gallop, *Ind. Eng. Chem.*, Vol. 16, pp. 1056–1062, 1924.) Chlorine gas was passed at low velocities through several such chambers in series.

At present, what little bleaching powder is made is produced by bringing chlorine into contact with dry hydrated lime in a rotating sheet-steel cylinder. (Badger, W. L., and E. M. Baker, "Inorganic Chemical Technology," 2d ed., McGraw-Hill Book Company, Inc., New York, p. 188, 1941.) This is set at a slight pitch and is provided with lifting baffles on the inside to shower the lime down through the gas. Some heat is evolved in the reaction. This is taken care of by radiation in cold weather and by water sprays on the steel shell in warm weather.

Packaging

The bleach is loaded in steel drums for shipment.

BUTADIENE

Butadiene is no problem to handle, but its production by the several processes does call for some special materials of construction. Much of the butadiene is made from alcohol and from petroleum.

Production

Materials of Construction.—Where alcohol is the raw material, the equipment is almost entirely plain carbon steel, no stainless is used, and a minimum of copper is to be found.

Alcohol Process.—Alcohol is pumped from storage tanks to the distillation system, where it is vaporized and passed into converters, vertical tubular vessels. The tubes contain the catalyst. Several of the converters produce acetaldehyde, which is then combined with the alcohol fed to the remaining converters. (Lee, J. A., GR-S Rubber, *Chem. & Met. Eng.*, Vol. 50, No. 6, pp. 98–102, 1943.) The product from all converters is cooled by heat exchangers and condensers. Uncondensed gas is scrubbed under pressure in order to recover materials. Condensate and scrubber liquor are combined and fed to a single set of continuous stills in which the butadiene and unreacted materials are purified. The butadiene is stored in spherical steel pressure vessels.

Handling

Butadiene can be handled by any of the commonly used materials of construction. Ordinary carbon steel and cast iron are generally used.

BUTTER

All dairy products are handled and processed with great care in order to prevent contamination for the sake of cleanliness and to avoid rancidity and off tastes.

Wooden churns have long been standard in the industry; however, some plants prefer aluminum churns, which can be cleaned and sterilized more easily.

Glass-lined steel is used in some dairies for vacuum deodorizing of cream to be used in butter making.

Large quantities of stainless steel are used. In the production of butter the question of metallic contamination is a problem which is eliminated by the use of 18-8 stainless steel. It has been found that, if cream were contaminated with copper to the extent of less than 1 ppm., the butter made from such cream would be affected. Such butter if put in cold storage for some months would rapidly develop a tallowy flavor on removal from the cold store. This fact gave an impetus to the change-over from tinned copper to 18-8 stainless-steel plant throughout the butter factories, and the cream separators used by the farmers were also brought into line by having the bowl assembly made from 18-8 stainless steel. (McWilliam, J. A., Use of Stainless Steel in Chemical and Food Process Industries, *Murex Ltd. Rev.*, Vol. 1, No. 1, p. 1, 1948.)

Nickel and nickel-clad steel are used for cutting machines and packing tables.

BUTYL ACETATE

Butyl acetate is used extensively in the manufacture of lacquers, artificial leather, photographic fiber, safety glass, and other preparations.

Production

Materials of Construction.—While much of the equipment can be fabricated of plain iron or steel, it is customary to use copper for stills and columns and in some plants to use valves of brass or bronze. The pumps may be cast iron with bronze fittings. Storage tanks are generally ordinary steel. In other plants Monel is used for kettle stills and heater tubes in distillation.

Batch Process.—Butyl acetate is made from pure normal butyl alcohol and acetic acid. The still is heated under reflux until the temperature at the top of the column becomes constant at about 89°C. (Groggins, P. H., "Unit Processes in Organic Synthesis," 3d ed., p. 655, McGraw-Hill Book Company, Inc., New York, 1947.) Then the distillate is withdrawn from the condenser as rapidly as possible without permitting the temperature to rise above 90°C.

The layers are separated in an automatic separator, the upper layer is returned to the still, while the lower is taken off and measured. As the reaction nears completion, the amount of water that separates diminishes until there is none; the temperature in the still flattens out at the refluxing temperature of the butyl acetate.

The crude acetate is cooled and neutralized with aqueous caustic soda. After separation of the water layer, the ester is ready for refining by distillation. The first fraction is the ester-water binary which is caught in an automatic separator, from which the ester layer is returned to the still. The next is a small fraction which contains some water. It is added to the next batch. The remainder of the distillate is finished ester and goes to storage.

Packaging

Butyl acetate is shipped in steel drums and tank cars.

BUTYLENE GLYCOL

A group of American engineers visiting German chemical industry immediately after the Second World War found that butylene glycol was made at Hüls by Chemische Werke of I.G. Farbenindustrie. (Handley, E. T., *et al.*, Synthetic Rubber Plant, Chemische Werke Hüls, p. 39, U.S. Department of Commerce.)

Production

Materials of Construction.—The reactor was made of a chromium-molybdenum steel and lined on the inside with copper.

Process.—Briefly, 1,3-butylene glycol is produced by the hydrogenation of aldol in continuous vertical reactors at 300 atm. and 50 to 150°C. over a catalyst made of 17 to 20 per cent copper and 0.7 to 1.0 per cent chromium on calcined silica gel.

Aldol is hydrogenated in vertical continuous reactors. The vessels are constructed for pressures of 300 to 700 atm., are of chromium-molybdenum steel, and are copper-lined on the inside. They are filled with the catalyst.

In starting up, the reactor is pressured with 100 atm. of N_2. About 7,000 cu. m. per hr. of gas is recirculated over the catalyst, and the reactor gradually heated to 200°C. Hydrogen is then introduced so as to have the reactor at 300 atm. and circulating gas at 80 per cent hydrogen and 20 per cent nitrogen. This is circulated until the catalyst is reduced to the active metals. The temperature is then reduced to 50°.

Aldol is heated in preheating coils to 50 to 70°C. and enters the reactor. Hydrogen is also passed in at the same temperature and 300 to 700 atm. and at the rate of 13,000 cu. m. per hr. to remove reaction heat. Both reactants pass down over the catalyst. The reactor is equipped with cone baffles every 2 ft. for liquor redistribution.

The reaction releases considerable heat and raises the temperature to 50 to 90° depending on the catalyst age. The reaction is carried to completion in one pass.

The product passes through a heat exchanger with incoming hydrogen, where it is cooled to 50 to 120°C. It then passes through a cooler, where it is further cooled and sent to a liquor separator, a slightly inclined horizontal vessel. The gas is separated and recycled with 1,100 cu. m. per hr. of fresh hydrogen 97.8 per cent pure, and the liquid products are sent to several separators at atmospheric pressures.

Crude butylene glycol is purified in two trains of four distillation columns each.

CALCIUM CHLORIDE

Calcium chloride comes from two sources, natural brine and waste liquors from the Solvay process.

Production

Materials of Construction.—Despite its long-held reputation as a corrosive material, calcium chloride does not present any serious corrosion problems in its manufacture. (Kreider, H. E., Calcium Chloride, *Chem. & Met. Eng.*, Vol. 41, No. 10, p. 518, 1934.) A good quality cast iron performs satisfactorily in most applications. Occasionally there are instances where graphitic corrosion gives trouble, *e.g.*, in pump parts. If the cause of the trouble cannot be discovered and removed, bronze parts can be substituted or some other corrosion-resistant materials used. Cast iron is generally recommended for the valves and cocks in a calcium chloride plant. Piping should be of wrought iron, preferably galvanized.

Calcium chloride evaporators are sometimes made of cast iron with the tube and tube sheets of ordinary steel. Corrosion trouble can be prevented to a large degree by avoiding leakage of air into the system. Concentrating pans can be made of sheet steel, but it is advisable to protect the metal on the inside by chemically resistant masonry set in acidproof cement.

Process.—Natural brine after purification or Solvay waste liquors as they come from the plant are concentrated first in multiple-effect evaporators and finally in a single-effect finishing pan until they reach 75 per cent solids. (Badger, W. L., and E. M. Baker, "Inorganic Chemical Technology," 2d ed., p. 214, McGraw-Hill Book Company, Inc., New York, 1941.) Both solutions contain sodium chloride, but this is only slightly soluble in strong calcium chloride solutions and, therefore, separate in the earlier stages of evaporation. The 75 per cent solution is run into drums or over a flaker. The flakes are usually passed through a direct oil-fired rotary calciner. This gives a thin coating of anhydrous calcium chloride, which is less hygroscopic. The flakes so treated are superior from the standpoint of storing and handling.

Monel evaporator bodies are used in some plants for evaporation of calcium chloride solutions to 60 to 70 per cent concentration. Heater tubes of the same metal are sometimes used, but Inconel tubes have shown satisfactory performance with lower corrosion rates as long as they are completely immersed in the solution. Monel can be used for scrubbers and air dryers. Monel evaporator tubes are used in evaporation of mixed calcium chloride and calcium chlorate. Inconel heater tubes are used in evaporation of mixed calcium and magnesium chlorides.

Handling

Cast Iron and Steel.—Corrosion may be expected but is usually slow enough to make plain iron and steel the most economical selection if iron contamination can be tolerated. They are frequently used. Inhibitors are useful in reducing corrosion. (Spitz, A. W., Corrosion Resistance of Steel and Cast Iron, *Chem. Eng.*, Vol. 54, No. 2, p. 135, 1947.)

An all-cast-iron pump is in use for handling a calcium chloride brine of pH 7 to 8. Such equipment as cast-iron reaction kettles, fusion kettles, and filter presses are used extensively in both handling and manufacturing. (Rother, W. H., Utilizing Cast Iron in Chemical Equipment, *Chem. & Met. Eng.*, Vol. 40, No. 7, p. 350, 1933.)

Stainless Steel.—In the dairy and ice-cream industries calcium chloride brine is often encountered as a cooling medium. Such brine tends to become acid and therefore more corrosive. It is advisable to keep it alkaline. For contact in the calcium chloride brine 18-8 Mo should be used. (McWilliams, J. A., Use of Stainless Steel in Chemical and Food Process Industries, *Murex Ltd. Rev.*, Vol. 1, No. 1, p. 1, 1948.)

High-alloy stainless steels such as Durimet 20 and Worthite are resistant at all concentrations and temperatures and are valuable in pumps where erosion-corrosion is involved.

Aluminum.—Much aluminum is satisfactorily used commercially in contact with inhibited, impure calcium chloride brine. The addition of sodium chromate in a concentration of about 1 per cent of the chloride content usually is sufficient to prevent attack of aluminum completely or almost by neutral impure chloride solution. (Aluminum Co. of America, "Aluminum in the Chemical Industries," p. 37, 1944.)

Nickel and Monel.—Both these metals are highly resistant to the brines used for refrigeration. Tests in calcium chloride brine tanks where no dichromate or other inhibitor was used have shown a rate of corrosion for both metals of less than 0.001-in. penetration per year.

Rubber.—Soft or hard rubber will handle solutions of calcium chloride up to saturation at 150°F.

Packaging

Calcium chloride solutions can be shipped satisfactorily in tank cars. Steel drums are generally used for the solid or fused product. Flaked calcium chloride is shipped in steel drums or in waterproof, paper-lined burlap bags in which a sandwich of asphalt is enclosed between the paper laminations. (Kreider, *loc. cit.*)

CALCIUM HYPOCHLORITE

Calcium hypochlorite can be made by any one of several methods, all of which call for special materials of construction to withstand the corrosion.

Handling

Concrete-lined wood tanks are used for the storage of calcium hypochlorite. Concrete with steel and cast-iron agitator parts is used for mixing, settling, and storage.

Hard rubber is in use. Special soft rubber is used up to saturation at 150°F. Rubber-lined tanks, pipe, and fittings using both natural and synthetic rubber have been used successfully for handling calcium hypochlorite.

Pyroflex linings are used for production and storage tanks. (Rauh, C. A., Pyroflex Construction for Acid and Alkali Service, *Trans. A.I.Ch.E.*, Vol. 35, pp. 463–472, 1939.)

Saran pipe and Saran-lined steel pipe are in use for handling this chemical.

Durimet 20 resistance depends upon many variables such as alkalinity, since free chlorine may be harmful.

High-silicon iron and Durichlor are widely used as pumps, valves, piping, etc., handling hypochlorite bleach solutions. Both alloys provide approximately equivalent resistance to solutions up to 15 per cent available chlorine, but Durichlor is the more satisfactory alloy above that concentration. Mixing nozzles of these alloys are often used for introducing chlorine into calcium hydroxide during manufacture of this bleach solution. Tests indicate that these alloys show comparatively little tendency to decompose the bleach.

Hastelloy C is resistant to strong hypochlorite solutions up to about 160°F.

Worthite pumps are in use with satisfactory results with calcium hypochlorite for bleaching textiles and paper. Recommendations for Worthite are calcium hypochlorite, cold 3½ per cent maximum available chlorine. Worthite is not recommended for use in manufacture of calcium hypochlorite in the concentrated form involving 15 to 23 per cent available chlorine.

Ordinary steel and cast-iron pumps and piping are in use. High-silicon iron pumps are used with this chemical. Glass-lined tanks are in use handling a 5 per cent solution at room temperature. Wood tanks are used when solutions are not always alkaline. For piping Transite, chemical porcelain and stoneware can be used.

Monel, nickel, and Inconel are frequently resistant in alkaline chlorine solutions such as calcium or sodium hypochlorite solutions used for bleaching and sterilizing purposes having available chlorine concentrations as high as 3 g. per l., in discontinuous operations, such as cyclic textile bleaching, where the bleaching cycle is followed by rinsing and acid "scouring" in the same vessel. (Friend, W. Z., Nickel, Nickel Alloys, *Chem. Eng.*, Vol. 54, No. 3, p. 213, 1947.)

In higher concentrations, attack is likely to be severe and accompanied by pitting. These materials are resistant to continuous exposure to the very dilute hypochlorite solutions, usually containing less than 500 ppm. available chlorine, used for sterilizing purposes. In the making of hypochlorite bleached paper stock, Monel is used for wire covers and other parts of vacuum washers and for lining the vats and repulper sections of the washers.

Stainless steel, Type 304, offers excellent resistance to corrosion in calcium hypochlorite solutions containing up to 3 per cent available chlorine for periods of exposure not exceeding 4 hr. The metal must be rinsed thoroughly with water immediately after use. Types 316 and 317, which are more resistant than Type 304 to attack by pitting, are the best grades for exposure to solutions of this kind. They have been used successfully for handling alkaline hypochlorite solutions containing 0.3 per cent available chlorine in equipment for entire bleaching cycles.

Coatings of some types have been successfully used. Vinyl resins were used in large quantity during the war to coat shipping containers. These finishes have been applied to the exterior and interior of containers used to ship the hypochlorite overseas.

Amercoat No. 33 has been used in the production of both calcium and sodium hypochlorite solutions. Prufcoat has been used as the protective coating over concrete in hypochlorite solutions. For low residual amounts of chlorine in portable water, Prufcoat has been successfully used on some occasions. The baked phenol-formaldehyde resins are not recommended.

CAPROLACTAM

Caprolactam is the raw material which was produced at the I.G. Leuna Werke for the manufacture of a nylon in its relatively high moisture absorption, which was reported to be as high as 20 per cent. The monomer was sold to the I.G. plants at Landsberg, Berlin-Lichtenberg, and Premnitz, which polymerized the material and spun it into fibers. (Boundy, R. H., and R. L. Hasche, Manufacturing of Thermoplastics of I.G. Farbenindustrie, No. 1069, Combined Intelligence Objectives Committee, G-2 Division, SHAEF (Rear) APO 413, U.S. Department of Commerce.)

Production

Materials of Construction.—Corrosion was a serious problem here. Therefore, not only ordinary steel autoclaves and other equipment were used but also lead-lined vessels, stoneware kettles, and stainless-steel kettles.

Process.—Briefly, the process consisted of the following reactions: (1) Phenol was reduced to cyclohexanol, (2) cyclohexanol was reduced to cyclohexanone, (3) this was reacted with hydroxylamine to form the oxime, and (4) the oxime was converted by sulphuric acid to the lactam.

Tar acids were distilled to separate pure phenol, which was reduced with hydrogen employing a nickel-aluminum oxide catalyst. Reduction was carried out continuously in an ordinary steel autoclave.

Cyclohexanol was dehydrogenated over a zinc-iron catalyst. Cyclohexanone was reacted at 70°C. with a hydroxylamine sulphate solution made from sodium nitrite and sulphur dioxide. Equimolar quantities of a 10 per cent solution of hydroxylamine and cyclohexanone were employed. The reaction was carried out in an agitated lead-lined vessel. The mixture was heated to 90°C. The reaction was exothermic, and cooling was required. The oxime separated as an upper layer and was removed in the molten condition from the aqueous layer, which contained ammonium sulphate.

Since the reaction of the oxime with sulphuric acid was exothermic, it was carried out in molten caprolactam. A kettle provided with means for cooling was filled two-thirds full with a solution of 95 per cent caprolactam and 5 per cent of 25 per cent oleum. One mole of the oxime to 1.05 moles of oleum was slowly added, and the product continuously withdrawn through an overflow.

Neutralization with ammonia was carried out in a stoneware kettle, adding the caprolactam hydrosulphite to a standard solution of ammonium sulphate. Sufficient water was added to maintain solution. The upper layer contained the caprolactam with 30 per cent water. It was decanted into a stainless-steel jacketed kettle. Water was distilled off at 300 mm. pressure and the caprolactam at 5 mm.

CARBON BISULPHIDE

Carbon bisulphide, or, as it is also known, carbon disulphide, has two important uses: in making viscose rayon and carbon tetrachloride. All other applications are minor as compared with these.

Production

Materials of Construction.—Electric furnaces are refractory-brick-lined. Retorts are sometimes made of low-alloy cast iron. One of the German plants used cast-steel retorts lined with fire-resistant tile. A life of 18 months was claimed for these retorts. Pumps generally have cast-iron casings and impellers with steel shafts. Piping is steel or wrought iron; valves and fittings are cast iron; condensers are steel or wrought-iron pipe and cast-iron fittings.

Process.—Carbon bisulphide is made by direct union of carbon and sulphur, either in an electric furnace or in a retort.

The electric furnaces have a shaftlike construction with the electrodes just above the hearth. Charcoal is fed into the furnace through the side walls. Some furnaces use fuel heat. Vapors from the furnaces are condensed with cold water, then they are redistilled.

Handling

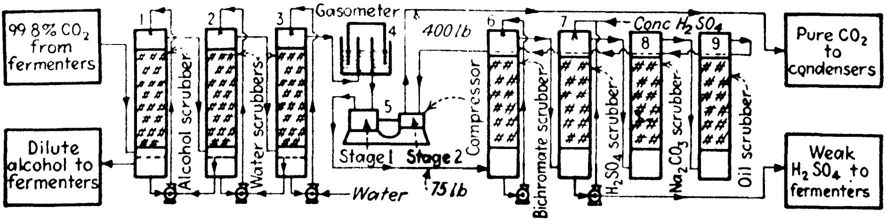
The commercial grade of carbon bisulphide is slightly corrosive to some metals owing to impurities. Tanks and containers used for storage corrode very little. This compound is generally handled by ordinary steel and cast iron.

Packaging

Carbon bisulphide is packaged in glass bottles or metal cans, steel or wrought-iron drums, galvanized and steel tank cars.

CARBON DIOXIDE

The derivation of CO_2 is stated to be from raw materials such as the fermentation of saccharine materials, molasses, and grain and from natural sources, such as natural-gas wells, but the largest amount of CO_2 is recovered from lime kilns



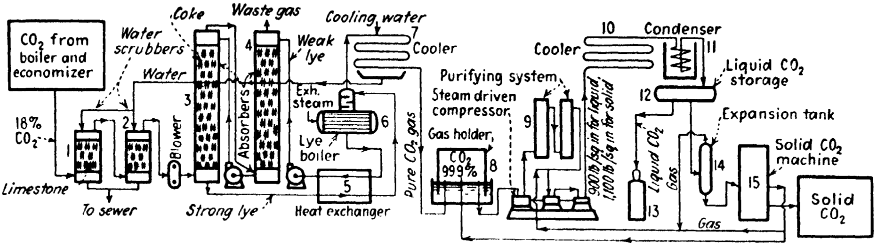
Fermentation CO_2 purification (Reich process).

1. Steel
2. Steel
3. Steel
4. Steel
5. Cast iron
6. Steel
7. Steel
8. Steel
9. Steel

Pumps: Bronze for water and bichromate, acid resistance for H_2SO_4

Pipe: Steel

Valves: bronze for water and bichromate; Acimet for H_2SO_4; steel for high-pressure gas and cast iron for low-pressure.



Carbon dioxide (solid or liquid).

1. Steel
2. Steel
3. Steel
4. Steel
5. Steel
6. Steel
7. Steel
8. Steel
9. Steel
10. Steel
11. Steel
12. Steel
13. Seamless steel
14. Firebox steel
15. Cast steel

and flue gases produced by burning a high grade of coke. (Reich, G. T., Alkali Slurry for CO_2 Recovery, *Chem. & Met. Eng.*, Vol. 47, No. 3, pp. 152–155, 1940.)

Carbon dioxide from fermentation products and natural sources requires only deodorization, since the CO_2 content is high. However, CO_2 in flue gases from coke or lime kilns varies from 17 to 40 per cent, and as these gases are contaminated with dust, etc., their use requires more complicated treatment before the CO_2 can be liquefied.

Production

Materials of Construction.—There are no problems in connection with the manufacture or handling of carbon dioxide. Ordinary steel is used for the equipment.

Standard Absorption Process.—Gases passing from the kiln are conveyed to scrubbers to remove dust and water-soluble materials. They are then blown to absorption towers. The two towers are connected in series for countercurrent flow of gas and lye solution. Strong lye solution is pumped to steam-heated boilers from the first tower. Lye boilers reverse the process of absorption, liberating purified carbon dioxide gas and returning "desorbed" lye solution to the system. The gas is cooled, then metered before passing into the gas holder.

Pressure of gas is raised in three-stage compressors to a point where the cooling effect of condensers will cause liquefaction. Later the liquid CO_2 is passed to an expansion tank of firebox steel. The snow is pressed and formed into dense, solid blocks by hydraulic presses of the cast-steel machine.

Handling

Carbon dioxide can be handled in ordinary steel.

Packaging

Steel is used for shipping CO_2.

CARBON TETRACHLORIDE

This chemical is made by several processes. In every case considerable corrosion is encountered due in part to the raw materials that are highly corrosive and also in part to the material itself which gives trouble when wet.

Production

Materials of Construction.—In the standard process of producing carbon tetrachloride by chlorination of carbon bisulphide, cast-iron equipment, owing to its low initial cost and its serviceability, has been extensively used. This is true particularly of the reaction and distilling equipment, up to the point where sulphur chloride is eliminated. Ordinary steel and wrought iron, although not particularly serviceable in the presence of heat and sulphur chloride, are widely and satisfactorily used for storage tanks for crude and finished carbon tetrachloride. For the finished material, glass-lined steel or lead- or tin-lined tanks would be preferable but on account of their greater cost are not so generally used.

In the production of finished carbon tetrachloride, lead condensers are recommended. Pumps and valves used in a carbon tetrachloride plant require careful attention from the standpoint of materials used in their construction. Cast-iron or stainless-steel valves of the gate type are generally most serviceable in this process. Cast-iron cocks have been used, but owing to the difficulty of lubrication, they tend to bind and are therefore not so satisfactory. The pump commonly used is supplied with a cast-iron casing and impeller and steel or cast-iron shaft. (Penfield, Walker, Carbon Tetrachloride, *Chem. & Met. Eng.*, Vol. 41, No. 10, p. 519, 1934.)

Chlorination-of-methane Process.—The process used to make carbon tetrachloride by the chlorination of methane at Hüls, Germany, has been reported. (Neubauer, J. A., High-Temperature Chlorination of Methane at Hüls, FIAT Final Report 1154, U.S. Department of Commerce, 1947.) This plant is essentially a hydrochloric acid plant which has been partially converted to make carbon tetrachloride and hydrochloric acid. The process operates smoothly and without difficulty.

The equipment used for the burning of methane and chlorine is the same equipment as used for the burning of hydrogen and chlorine except that a small combustion chamber of brick-lined steel is added. The burners are horizontal and are constructed mainly of lead, and, except for the hydrogen and chlorine inlets and the short combustion chamber, the equipment is submerged in water. The combustion chamber is attached to a lead pipe. The opposite end of this lead pipe is drawn down, and to this small diameter is attached a horizontal coil of lead pipe. The pipe and coil are immersed in a rectangular steel box filled with water.

The mixed gases are introduced through a quartz tube into the combustion chamber. A group of long glass tubes in parallel are used. They are externally cooled with water, and the water is introduced at the top to absorb the hydrogen chloride and condense the chlorinated hydrocarbons. The neutralizer consists of a small tank, a second small tank for a separator, and a pump. All this equipment is iron. The lead-lined still and column adopted for this purpose is packed with raschig rings.

Before the gases enter the burner, they must be premixed. This is done by introducing the chlorine and methane at the bottom of a small tower packed with rings.

The mixed chlorine and methane are burned in two stages. In the first stage 100 per cent excess chlorine is added. This excess chlorine acts as a diluent. Chlorine and methane are added to the first burner. In the first stage the gases burn at about 500°C. The gases leaving the lead cooling coil of the first burner (at about 30 to 40°C.) are mixed with methane and enter the second burner. The temperature in the second burner is somewhat lower than in the first burner. The hydrogen chloride gas from the first stage acts as a diluent in the second-stage burner. A cold burner is brought up to temperature by starting it on hydrogen and chlorine. When the combustion chamber is hot, the hydrogen is shut off and methane turned on slowly. The gases from the second-stage burner are then sent to the absorption system, where a 30 per cent hydrochloric acid solution is produced and the chlorinated hydrocarbons are condensed.

The hydrochloric acid, after decanting the chlorinated hydrocarbons, contains some chlorine and chlorinated hydrocarbons, but it is used as such without further purification in this plant. The waste gases containing chlorine are vented to the atmosphere. Approximately 7 to 10 per cent of the chlorine added is excess and wasted.

The chlorinated hydrocarbons from the decanter are neutralized with a 30 per cent caustic soda solution. This neutralized mixture of chlorinated hydrocarbons is then steam-distilled, and the heavy fractions separated as still residue.

The product from the still is again separated from the water and is poured into drums without further treatment. This product contains approximately 20 per cent perchlorethylene and 80 per cent carbon tetrachloride. The crude product contains about 2 to 3 per cent hexachlorethane.

Handling

Both plain cast iron and steel can be used satisfactorily with carbon tetrachloride provided it is dry, but if water is present, other materials such as glass-lined steel must be used for handling it. Water hydrolyzes tetrachloride slightly to form hydrochloric acid.

Illium in boiling CCl_4 shows no more than 0.004-in. penetration per year. Worthite pumps, valves, and other equipment are in actual service handling this chemical. It can be stored in wood and lead-lined vessels. Bronze is said to resist it even when water is present. Durimet 20 is resistant at all temperatures. Carbon tetrachloride does not attack silver equipment.

HCl, which sometimes forms when water is present with carbon tetrachloride, has a corrosive action on aluminum; this action is more severe at elevated temperatures.

A fibrous form of Teflon has been developed that can be molded with a small percentage of binder to yield a packing ring suitable for high-speed pumps. Since the amount of binder required rarely exceeds 7 per cent, the chemical resistance of the ring is excellent. These packings have been used with excellent results on pumps handling CCl_4. (*Chem. Eng. Progress*, Vol. 44, No. 1, p. 89, 1948.)

If removed from the original containers, carbon tetrachloride should be stored in tinned, galvanized-iron, copper, lead, Monel, glass-lined steel, or nickel containers. Storage in black-iron containers may result in corrosion. (Manufacturing Chemists Association, "Carbon Tetrachloride," Chemical Safety Data Sheet SD-3.)

When free from water and at atmospheric temperature, chlorinated hydrocarbon solvents are not corrosive and steel equipment ordinarily can be used to handle them. However, in the presence of entrained water or a water layer and particularly at elevated temperatures, such as we encountered in the distillation and recovery of the solvents, there is appreciable hydrolysis with resulting formation of dilute hydrochloric acid. The development of acidity is accelerated by light and air. Under such conditions steel frequently is rapidly attacked. Over a period of many years' service Monel and nickel have shown a high degree of resistance to corrosion under these conditions with a wide variety of chlorinated hydrocarbons. Both materials are used for distillation and recovery equipment in the manufacture and application of the solvents. (International Nickel Co., *Tech. Bull.* T-29, 1945.)

Packaging

Carbon tetrachloride is usually shipped in tinned cans, galvanized-iron drums, or steel tank cars.

CASCARA

The cascara tree grows only in the Northwest's rain belt. About 100 lb. of the bark will give some 23 lb. of the concentrate. The concentrate is now made to a large extent on the West Coast and shipped to pharmaceutical manufacturers in all parts of the country.

Production

Materials of Construction.—Steel is used for percolators and some other equipment. Stainless steel is used for the spray dryer and piping.

Process.—Bark from the cascara trees is ground, sacked, and aged for 1 to 2 years in a room where air is circulated freely. (Bloomberg, R., Botanicals, *Chem. Eng.*, Vol. 56, No. 4, pp. 108–109, 1949.) It is then mixed with water and—where specified—magnesium oxide is added as a debitterizing agent. The wet mixture is spread on an acid-resistant floor for 24 hr. to macerate and complete the debitterizing action.

The mixture is then placed in a steel percolator with a capacity of 800 lb. of bark. Steam is fed in under slight pressure to keep the water at 212°F. for 2 hr.

Thin "percolate" is piped to a holding reservoir, then to evaporators where it is reduced to 25 per cent solids. A centrifuge removes insoluble material.

A high-pressure pump—capable of 5,000 psi. but usually operated at 3,000 to 4,000 psi.—forces the concentrate from the holding tank to the top of a stainless-steel spray dryer similar to the type used for whole milk. The mixture is forced out of the atomizing nozzle into a chamber where air at 250 to 300°F. enters from the sides at the rate of 7,500 cu. ft. per min. Moisture is evaporated almost instantly. The dried solids drop into an 8-in. stainless-steel pipe and are blown by a high-velocity fan into a small cyclone, where the solids are separated from the air.

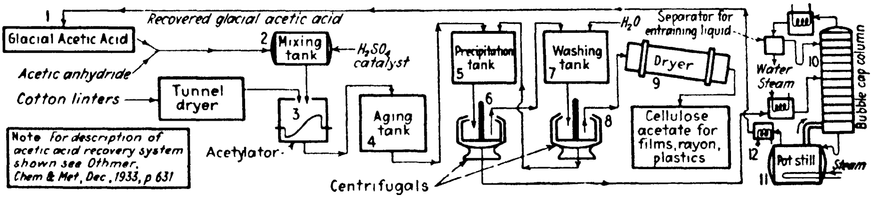
Exhausted air from the cyclone passes into a second chamber and finally into a fines collector; both are connected with the packaging room by the same pipe that serves the first cyclone.

Packaging

The final concentrate is packaged in moistureproof lined barrels of 50-, 100-, and 200-lb. capacity.

CELLULOSE ACETATE

The production of cellulose acetate calls for special materials of construction. The acetic acid, acetic anhydride, acetone, sulphuric acid, and other chemicals used in its production attack ordinary materials. Some metals must be avoided, for they affect the color or surface of the fiber or plastic product made from the cellulose acetate-base material.



Note For description of acetic acid recovery system shown see Othmer, Chem & Met, Dec, 1933, p 631

Cellulose acetate.

1. Aluminum
2. Aluminum
3. Copper-lined, stainless steel, bronze
4. Bronze, stainless steel, glass-lined steel
5. Wood, aluminum, bronze, stainless steel
6. Aluminum, stainless steel
7. Aluminum, wood, stainless steel
8. Aluminum, stainless steel
9. Aluminum, stainless steel
10. Copper with bronze caps, etc., Type 316 stainless steel
11. Copper with Herculoy, Everdur, or copper tubes
12. Type 316 stainless steel, silver

Production

Materials of Construction.—Much equipment used in the preparation of cellulose acetate is fabricated of aluminum alloys. This includes precipitators, centrifugal dryers, continuous screen dryers, and rotary dryers. By means of aluminum equipment, the whiteness of the product can be maintained.

Stainless steel is used extensively in some acetate plants. Stainless-steel equipment includes pretreaters for the cellulose with glacial acetic acid, piping, acetylator, perforated belt in the washer, and the spinneret nozzles.

High-silicon pumps and valves handle the sulphuric acid. Durimet or Worthite valves, pumps, fittings, and tank outlets are used for handling acetate slurry and for other purposes. At least one plant is known to be using a bronze hydrolysis vessel. Wooden tanks are sometimes used for construction of precipitators. Wooden hoppers for holding the dried linters are customary. At least one manufacturer uses a copper-lined acetylator. Galvanized iron is used for the linters, for holding the wet flakes after acetylation, and for other purposes. Glass-lined steel can be used for hydrolysis.

The greatest use of corrosion-resisting equipment is in the recovery of the chemicals, especially acetic acid and acetic anhydride. The use of copper is looked upon with skepticism by some engineers because of the ill effect of copper contamination on the luster and dyeing properties of yarn.

In these systems a great deal of stainless alloys is used as piping, fittings, valves, pumps, and special castings, as well as high-silicon iron valves and drain lines.

In the recovery of acetone, stainless steels are used in quantity to prevent contamination, but corrosion is relatively mild.

Process.—The production of cellulose acetate is fundamentally simple. Wood pulp is fluffed and packed into aluminum pans. The pans of pulp are slid along on a roller conveyor into the steeping room, where a measured volume of acetic acid is added through a sprinkler. The pulp is then stored in a conditioning room for carefully controlled aging. After aging, it is charged into kneading machines and acetic anhydride, glacial acetic acid, and sulphuric acid (the catalyst) are added. A viscous solution, "acid dope," is the product of this operation. It is now emptied into stainless-steel or glass-lined tanks called "eggs" in which it is aged for a definite length of time.

The eggs are then tilted, and the dope is emptied through pipes into big precipitating tanks. Here the acetate is precipitated from the acid dope by acid baths and a final water bath. After the acid is drawn off, the cellulose acetate is dropped into a tank known as a "hot vat" or stabilizer where hot water and acid remove any impurities that may be present. The material now goes over a screen where the cellulose acetate is separated from the hot water. The wet acetate is fed into a dryer from which it emerges in granular form. Several batches of acetate are blended together. The uniform material is placed in a mixer and dissolved in acetone to form spinning dope. It is forced through a series of high-pressure filters, where all undissolved material is removed by dense filter packs of cellulose material. It is then pumped into tanks and is ready for spinning.

The spinning operation is in a vertical direction downward from the top of the machine to the spindles at the bottom of the machine. The spinning dope is drawn from the spinning tanks and is forced through pipes to the spinning machine. Each spinning machine is made up of a number of units designed to produce one thread. Each unit is composed of a measuring pump, spinneret, hollow tube for evaporation, and a motor-driven spindle carrying a bobbin for the yarn.

As the filaments of dope travel downward through the cylinder, a current of warm air evaporates the acetone from them and carries it off. By the time the filaments reach the spindles, they are solid and dry and form a finished yarn.

Recovery of Chemicals.—The liquor drawn from the precipitated flake cellulose acetate contains a considerable amount of acetic acid in dilute form. This results from dilution of glacial acetic acid as well as from hydration of acetic anhydride. A portion of the precipitation liquor is carried to a still in which the pure acid is separated from water and impurities, after which it is reused in the production process.

The balance of the diluted liquor from the precipitation process is treated with soda ash to precipitate sodium acetate. The dried precipitate is then treated with sulphur dichloride to form acetic anhydride. Following this, concentration and purification are carried out by distillation.

Acetone is returned from the spinning end of the process diluted with air. One method of recovery consists of absorption in alternate closed vessels containing activated carbon. When the carbon is loaded with acetone, the flow is switched to another vessel and the acetone removed with dry steam. A rectifying still discharges the acetone from the top of the column through a condenser.

CELLULOSE NITRATE

The strong mineral acids used in the production of cellulose nitrate demand stainless steels and other special materials of construction.

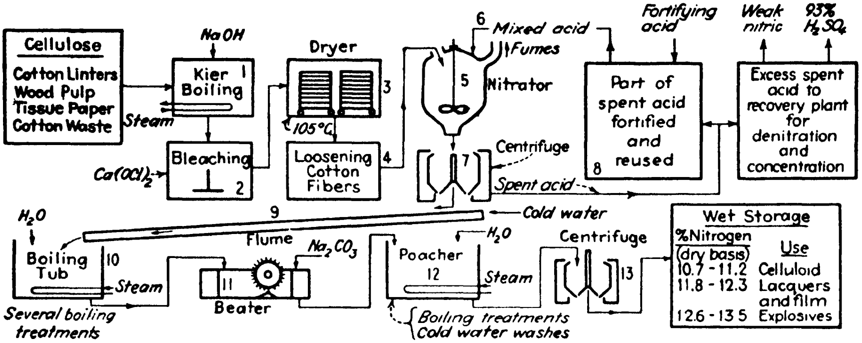
Production

Materials of Construction.—Types 304, 316, and 430 stainless steels have been found to be satisfactory for mixtures of sulphuric acid and nitric acid such as are encountered in nitration of cellulose. Plain carbon steel can be used for some pieces of equipment. Chemical stoneware and wood are used to a limited extent. Aluminum flume ducts, ventilating hoods, washing tanks, and centrifugal extractors have been used.

Process.—Cellulose nitrate is used for several purposes and is made by several methods depending upon the use for which it will be put.

In one plant which digests the cellulose nitrate in water, the mixed nitrating acid is handled in steel piping, fittings, and pumps. Since there is a closed system, there is no chance for air to enter or water to collect. The acid and cotton linters enter a nitrator. This vessel, the agitator, and fittings are made of Type 304, 316, or 430 stainless steel. The nitrated cellulose passes to a centrifuge. The basket is ordinary steel but would be better if it were Type 347 stainless steel. The spent mixed acid leaving the centrifuge is handled in ordinary steel pipe and fittings. The pump is Type 304 stainless steel. The nitrated cotton is drowned with water in wooden boiling tubs. These tubs are lined with Type 316 stainless steel. The washed cellulose is conveyed by a pump with Type 304 or 430 stainless-steel casing and impeller to the digester.

Formerly a batch process was used. Chrome-alloy equipment was used for small lots, and steel autoclaves lined with acidproof brick for larger units. The continuous system which replaced the batch method is a pipe line of chrome-steel tubing in numerous sections connected by long-sweep return bends. Next the material goes to wash tubs of Type 316 stainless-steel-lined wood. The cellulose nitrate is then dehydrated and shipped.



Cellulose nitrate.

1. Steel
2. Type 304 stainless steel
3. Steel
4. Steel
5. Type 304 or 316 stainless steel
6. Steel
7. Steel, Type 347 stainless steel
8. Steel
9. Terra cotta, Type 304 stainless steel
10. Wood lined with Type 316 stainless steel
11. Stainless steel
12. Steel
13. Steel

In the preparation of the cellulose nitrate for smokeless powder the nitrated cotton is separated from the spent acid in a plain steel or stainless-steel centrifuge, washed in wooden boiling tubs, run out of the tubs, and put into another intermediate slurry tank. Any free acid is neutralized with soda ash. The alkaline slurry is passed through a series of steel Jordan refiners and pumped by a steel pump to the poacher house. Final neutralization is accomplished here by addition of more soda ash. The residual ash and salts are removed by washing in the steel vessel. Cellulose nitrate is then ready for blending and finishing operations.

The Thomson displacement process used in Canada and elsewhere during the First and Second World Wars utilizes large stoneware nitrating pans.

CHLORACETIC ACID

This acid is made by the Germans by hydrolysis of trichlorethylene with water in the presence of sulphuric acid. (Adams, D. A. W., and W. Baird, Some Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.)

Production

Materials of Construction.—There are three separate units. The main plant items of each are

1. A reactor comprising a jacketed cast-iron pan with feeds to the bottom of the pan and an overflow (to storage tank) near the top. The trichlorethylene is led to the pan via a lead pipe, and the sulphuric acid via a glass tube.
2. A series of three gas-fired cast-iron vacuum stills each carrying a ring-packed column. Vacuum is by steam ejector. The series is arranged in cascade form.

Process.—Trichlorethylene and 73 to 75 per cent sulphuric acid are fed to the reactor via meters. The temperature is maintained at about 137° in the middle of the reactor (average temperature 130 to 140°C.), and the conditions are such that the emerging liquid contains 1 to 2 per cent water.

The emerging product contains about 50 per cent chloracetic acid and runs to storage. Glass-lined steel is satisfactory. The hydrochloric acid by-product passes to a ring-packed scrubber, where it is washed with trichlorethylene; the wash liquor is fed into the trichlorethylene being processed. The washed gas passes to a water cooler then to a brine cooler; the condensate is again fed to the trichlorethylene being processed: the hydrochloric acid gas then passes to another plant for making methyl chloride.

The chloracetic acid-sulphuric acid mixture is pumped to the first still; the still residue flows continuously to the second still and thence to the third. Each still operates at about 15 to 20 mm. Hg measured on the still body; the temperature of the first is maintained at 140°C. (liquid temperature), the second at 160°C., and the third at 180 to 193°C. The still vapors are combined in a common vapor line and are condensed in a condenser maintained at 68°C., about 4° above the melting point of chloracetic acid. The condensate is run to a heated receiver or to a flaker as required. The vapors emerging from the condenser are washed with water in a glass, ring-packed scrubber, and the wash liquor, containing about 5 per cent chloracetic acid, goes to dilute the sulphuric acid used in the process.

The residual sulphuric acid emerging from the last still contains about 6 to 7 per cent chloracetic acid and 2 per cent water; four-fifths are returned to the process, and one-fifth goes to drain to avoid build-up of impurities, losses being made up by addition of fresh acid.

Handling

Nickel tanks are used to store the acid solutions. The flaker drums handling molten chloracetic acid are nickel.

Packaging

Glass-lined steel tank cars are used for shipping.

CHLORACETIC ACID SODIUM SALT

Germany produced chloracetic acid sodium salt in the I.G. Farbenindustrie's plant at Höchst. The manufacturing process has been reported. (Adams, D. A. W., and W. Baird, Some Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.)

Production

Materials of Construction.—The equipment comprises essentially an open rectangular wooden vessel with a series of wooden rollers carrying iron spikes to act as mixers.

Process.—Chloracetic acid sodium salt is made by continuous reaction of the acid with soda ash. Liquid chloracetic acid and soda ash are fed to the wooden vessel, the ash going through a simple slit distributor at the end of the vessel where the acid is run in. The product is discharged from the opposite end by a worm conveyor into wooden barrels. It contains 1 to 2 per cent free acid.

Packaging

It is packaged in wooden barrels for shipment.

CHLORAL

A continuous process for the production of chloral, an important material for making DDT, dichlorodiphenyltrichlorethane, has been developed by A. Brothman. (Callaham, J. R., DDT Fights Insects in War and in Peace, *Chem. & Met. Eng.*, Vol. 51, No. 10, pp. 109–114, 1944.)

Production

Materials of Construction.—Alcohol, sulphuric acid, and muriatic acid storages are constructed of mild-steel plate. The muriatic acid storage has a Pyroflex backup layer covered by a single course of chemical brick. It contains Karbate heat-exchange surface as internal coils so as to maintain the acid at constant temperature and strength and back pressure on the hydrogen chloride absorber at a fixed value. The catalyst mixing tank is chemical stoneware with an air-lift agitator unit of Karbate gas-diffuser elements.

Process.—Chlorination of alcohol to chloral alcoholate is catalyzed by iron dissolved in HCl. Alcohol is fed continuously to the chlorinator bank. Reactors are arranged for countercurrent flow of chlorine through the bank. Gas for the third reactor is drawn from a recycle line off the vapor section of the first reactor. The second reactor draws its gas-lift fluid from the third reactor; the first vessel from the second. Free chlorine is fed through automatic feed-control vaporizing equipment to the last reactor.

The chlorinators are vertical tanks of mild-steel plate lined in the same manner as the muriatic storage. All have chemical stoneware, open-top draft tubes with Karbate gas-diffuser elements.

Chlorinated "oil" from the last reactor contains free chloral and other chemicals. In the acidulator this oil is mixed with 96 per cent sulphuric acid, which "degenerates" residual alcohol and completes the freeing of chloral from chloral alcoholate.

Acidulator feed consists of chlorinated oil and sulphuric acid. The acidulator is a mild-steel-plate tank lined with chemical brick in the same manner as the chlorinators. Chemical stoneware open-top draft tubes are provided. The unit is provided with an internal heat exchange.

Acidulated oil is sent to fractionating columns to remove side-reaction impurities. The columns consist of chemical-stoneware sections and are packed with Berl saddles. Chloral, coming off the top of the fractionating column, is sent to a storage tank.

Handling

Chloral can be stored in tanks constructed from mild-steel plate.

CHLORBENZALDEHYDE SULPHONIC ACID

A British team of engineers investigating the German chemical industry after the war reported that I.G. Farbenindustrie was producing 4-chlorbenzaldehyde-2-sulphonic acid. (Adams, D. A. W., and W. Baird, Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.) This product is made from 4-chlortoluene-2-sulphonic acid by a somewhat complex oxidation process. The product is isolated as a manganese salt.

Production

Materials of Construction.—A tile-lined kettle is used as a reactor. The oxidation kettle is a jacketed, lead-lined vessel. Either tile or lead is used for much of the other equipment. Glass-lined steel also is satisfactory.

Process.—Water and moist manganese carbonate containing about 40 per cent water are charged to a jacketed, tiled kettle with a gate stirrer. In the first phase of the reaction MnO_2 is formed from the permanganate and manganese carbonate, and in the second phase, at an elevated temperature, the dioxide reacts with sulphuric acid and an equivalent of divalent manganese to form manganic sulphate. As there is always a loss of oxygen in the reaction, a 5 per cent excess of $KMnO_4$ is used.

After charging the permanganate, the mixture is heated to 60°C. Half the total Mn is changed to MnO_2 which is present in a very finely divided form. A further quantity of 66°Bé. sulphuric acid is now run in, and the charge blown to the oxidation kettle, where it is heated and stirred; it is then allowed to cool. The manganic sulphate paste is diluted with water until a filtered sample shows a sulphuric acid strength of 56 per cent.

The oxidation kettle is a jacketed pan, lead-lined with tiles on top and provided with a lead-covered gate stirrer. Water and 66°Bé. sulphuric acid are charged to a jacketed kettle (tiled on top of lead) provided with a lead-covered gate stirrer. The chlortoluene sulphonic acid is added, the slurry heated, and air blown through until the small amount of hydrochloric acid arising from salt in the sulphonate has been expelled. This is necessary to prevent formation of hypochlorous acid during the oxidation.

The suspension is blown over to the oxidation mixture in the oxidation kettle, the temperature being kept below 40°C. The mixture is now heated at a uniform rate to 120°C. A rapid increase in temperature sets in at 45 to 50°C., and it is necessary to control this by cooling. The batch is stirred at 120°C. and should turn a straw yellow color. The manganic sulphate is consumed. The temperature is now reduced as rapidly as possible to 80°C. and then slowly during 3 hr. to 15 to 20°C., the acid concentration being at the same time adjusted to 64 per cent H_2SO_4 by addition of water. An addition of 100 kg. of sodium sulphate is also made to assist separation of the aldehyde sulphonic acid. The product is now filtered off and sucked as dry as possible on the nutsche.

The nutsche cake of manganese salts is transferred to a tiled vat provided with a heating coil, where it is mixed with water and heated to effect solution. The solution is then allowed to crystallize while stirring and cooling; the manganese sulphate remains in solution; the bulk of the aldehyde sulphonate separates out and is filtered off.

CHLORETHANE SULPHONIC ACID SODIUM SALT

At the Höchst plant of the I.G. Farbenindustrie, Germany produced the sodium salt of β-chlorethane sulphonic acid. (Adams, D. A. W., and W. Baird, Some Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.)

Production

Materials of Construction.—In one case a copper still was used, and in the other a lead-lined pan.

Process.—Two slightly different methods were in use.

In one process ethylene dichloride, sodium sulphite crystals, methanol, and water were charged to a copper still and refluxed for 22 to 24 hr. until the sulphite was consumed. The operating temperature was about 70°C. The excess ethylene dichloride and the methanol were then distilled off up to a liquid temperature of 102°C. leaving a 14 to 16 per cent solution of the chlorethane sulphonic acid sodium salt.

In the other process ethylene dichloride, sodium sulphite (100 per cent), and water were charged to a lead-lined pan provided with a lead heating coil. These materials were reacted together for 48 hr. at 90 to 95°C., the pressure being about 2 atm. Subsequent procedure was as above described.

CHLORIDES—SULPHURIC ACID

Carbon, glass-lined steel, graphite, and Karbate materials have proved satisfactory for service with mixtures of sulphuric acid and chlorides.

CHLORINATED POLYVINYL CHLORIDE

Two processes were in use in Germany for the manufacture of chlorinated polyvinyl chloride, one dealing with solvent, the other with suspension chlorination. The I.G. Farbenindustrie used both methods at Rheinfelden. (Ruebensaal, C. F., Chlorinated Polyvinyl Chloride, FIAT Final Report 1071, Technical Industrial Intelligence Division, U.S. Department of Commerce.)

Production

Materials of Construction.—Lead was used entirely for the equipment in both processes at this plant. However, I.G.'s Bitterfeld plant used considerable acid-resistant brick linings for the equipment.

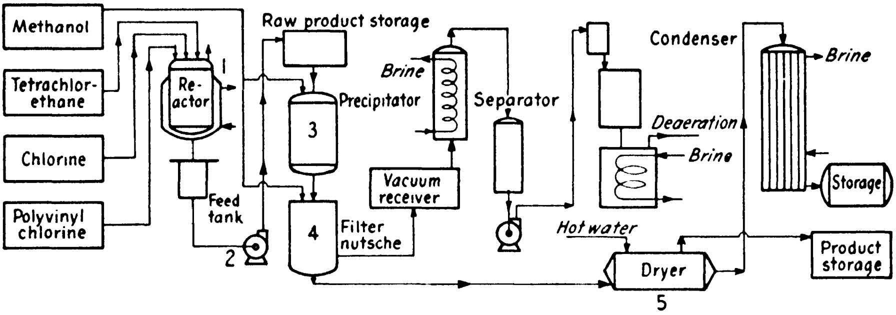
Solvent Process.—The weighed polyvinyl chloride powder was shoveled into the reactor into which the tetrachlorethane had been previously proportioned by a volume measurement. This lead-lined steel reactor was equipped with a plate-type stirrer. A steam jacket was utilized to bring the solution to 60°C. at which temperature the polyvinyl chloride went into solution. (A lead-pipe immersion coil was used at Bitterfeld.) Chlorine had to be added at this point, or the solution would rapidly turn brown. The chlorine was passed, in the gaseous state, to the bottom of the reactor through two lead tubes, which are slotted at the bottom to provide more equal distribution of the chlorine. The solution was brought to 90° after it was saturated with chlorine. As the reaction was exothermic, the temperature rose very rapidly to 120°. Water was circulated in the jacket as a coolant at this point, as the temperature could not be allowed to rise above 120°.

The Bitterfeld product was used mainly for fibers, and therefore the degree of chlorination that would yield the highest softening point was desired (K value about 56). The Rheinfelden product was employed for lacquers and adhesives, and therefore the desideratum was maximum solubility (K value about 30). In order to control the end product for the particular use to which it was to be put, an intermittent check on the degree of chlorination had to be made.

The progressive chlorination of polyvinyl chloride is similar to that of paraffin wax, which goes through a minimum viscosity range and then increases again as the chlorine content increases. This range for polyvinyl chloride is 63 to 68 per cent chlorine and was determined by a simple gelatination test at Rheinfelden.

When the reaction was determined complete, the clear, amber, siruplike liquid was conducted by gravity to a constant-head feed tank. From here it was pumped by a bronze centrifugal pump to raw-product storage tanks, one-half of the batch going to each of the two holders. Each of the raw-product storage tanks discharged into one of the two precipitation tanks. These were also steel vessels that had the lead lining faced with acid-resistant brick. They were also equipped with large-area, paddle-type stirrers. Methanol was stirred slowly into each half batch to lower the viscosity and thus permit better heat transfer. This reduction of viscosity is required, as it is necessary to cool the batches through the medium of a brine cooler to −10 to 12° before initiating precipitation.

As the batch approached −10°, methanol was slowly added from a storage tank, which in turn was fed by pump from recycle or stock methanol storage. The methanol was added in a thin stream until the batch assumed a spongy, curdlike consistency. The operator had to be careful to observe this formation as it was necessary to add the remainder of the methanol quickly at this point.



Chlorinated polyvinyl chloride.

1. Lead-lined steel
2. Bronze
3. Lead-lined steel faced with acid-resistant brick
4. Acid-resistant brick-lined
5. Nickel-plated cylinder and nickel tubes

The exit lines used to deaerate the precipitation tanks were small. Vacuum was applied to draw off part of the residual chlorine and hydrogen chloride gases before precipitation started.

The tetrachlorethane-methanol solution containing the suspended PC (chlorinated polyvinyl chloride) precipitate was next run by gravity feed from the precipitation tanks to an acid-resistant, brick-lined nutsche filter. Vacuum was applied to the bottom of this porous filter which caused the tetrachlorethane-methanol mixture to be drawn off of the PC cake and over into the 8.5-cu.m. vacuum receiver.

While the PC cake is still cold, it must be washed with 1,400 gr. of methanol. If this first wash is not made before the cake gets warm, fusion of the particles results. After this first 1,400 kg. of methanol wash was drawn off into the vacuum receiver, another 1,400 kg. of methanol was added and allowed to stand for a short time. The cake was sometimes broken up with a hoe at this point to ensure better washing. After the last wash was finally drawn off, the PC was ready for the dryer.

The transfer of the PC from the nutsche to the dryer was a manual operation. The dryer was a nickel-plated cylinder revolving on a horizontal axis and containing nickel tubes heated to 80° with hot water circulated by pump. Here the residual methanol was removed by means of heat and reduced pressure of 200 to 100 mm. Hg. The methanol evaporated from the dryer was reclaimed in a condenser.

The free-flowing, white, granular powder was dumped from the dryer into a hopper. Here it was ready for packaging for application work.

Suspension Chlorination Process.—Chloroform was pumped into a premixing tank equipped with a paddle-type agitator. The polyvinyl chloride powder was shoveled in. A small volume of chloroform was distilled off after the resin was wetted. The cold suspension was then fed to a horizontal, lead-lined autoclave, jacketed for temperature control. It rotated at 3 rpm.

After the reactor was charged with 75 to 80 kg. of liquid chlorine, it was heated to 92°C. Pressure increased to 4 atm. The temperature rose to 120°C., and the pressure to 12 atm. The reaction was terminated in 5 hr., when the temperature dropped to 40° and the pressure to 3 atm.

Air pressure forced the sirup over to a paddle-equipped neutralizer tank. At this point 3.8 kg. of potassium carbonate was introduced for neutralization. Pressure was released suddenly in the tank to permit escape of gases.

Three pressure storage tanks were used. The 10 per cent solution of PC in chloroform was blown by air pressure to a spray nozzle located in the base of the precipitator. Here steam projected the solution into a lead-lined column filled with a dilute solution of potassium carbonate.

Steam evaporated the chloroform, depositing the PC as a fluffy white precipitate in the alkaline water. This was passed into a side arm located halfway up the unit and then out into a U tube. The first leg of the tube was fitted with a rotating nickel-plated screw, which compacted the precipitate as it was carried down and over to the second leg of the U tube. The material was finally discharged from this side arm as a slurry into a screening vessel. It was given a water wash.

The product, which now contained 15 per cent water, was fed to a pelleter. It squeezed the water out and compacted the material to pellets. These were dried in a forced-air draft on trays at 60°C.

Packaging

The chlorinated polyvinyl chloride was packaged in paper bags.

CHLORINE

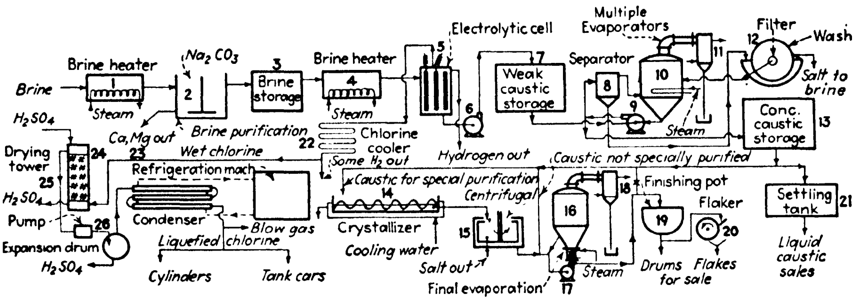
Chlorine when wet causes a great deal of trouble from corrosion due to the formation of hydrochloric acid but when dry can be handled by ordinary materials of construction. It is one of the most widely used chemicals; therefore the problem of its corrosion is one of the most important.

Production

Chlorine is made mostly by electrolysis of salt. Some is produced by other processes, such as in the manufacture of potassium hydroxide, metallic sodium, synthetic sodium nitrate, and electrolytic soda ash. Some chlorine is recovered from by-product hydrochloric acid in electrolytic cells.

Materials of Construction.—The brine feed to the electrolytic cells in the electrolysis of salt is heated in nickel or Monel tanks, treated with carbonate in a plain steel or rubber- or brick-lined steel tank, and stored in mastic-lined concrete. The diaphragm cell is steel with a soapstone or concrete cover; mercury cells are rubber-lined steel. Wet chlorine from the cells is handled in glass, chemical stoneware, or porcelain, and dry chlorine in plain steel.

Electrolytic Process.—Chlorine is produced in electrolytic cells. Brine is brought to the plant by cast-iron pipe lines, while rock salt is delivered in railway cars and stored in concrete tanks. The salt is dissolved in concrete, rubber- or brick-lined steel tanks. At a German plant raw brine was stored in outdoor



Electrolytic caustic soda and chlorine.

1. Nickel, Monel
2. Plain steel, rubber, or brick-lined steel
3. Concrete, mastic-lined
4. Nickel, Monel, steel
5. Steel tanks with concrete or soapstone cover for diaphragm; rubber-lined steel for mercury cells
6. Steel
7. Steel, nickel-clad steel
8. Steel, nickel-clad steel
9. Steel, Worthite, Ni-Resist, nickel
10. Bodies of 3 per cent nickel iron, nickel-clad steel, or lined with nickel sheets; nickel tube sheets and tubes
11. Steel
12. Nickel screen; Ni-Resist castings
13. Nickel-clad steel, nickel-lined steel
14. Bodies of nickel-clad steel or lined with nickel sheets; shafts and agitators of nickel
15. Monel baskets and wire-cloth liners
16. Bodies of nickel-clad steel or lined with nickel sheets; nickel tube sheets and tubes
17. Nickel, Ni-Resist
18. Steel
19. Cast iron, nickel cast iron
20. Ni-Resist drum; all other surfaces nickel
21. Nickel-clad steel, nickel-lined steel, plain steel
22. Glass
23. Stoneware
24. Stoneware
25. Plain steel
26. Steel

tanks made of steel lined with sheets of Oppanol (polyisobutylene) protected on the inside by a course of acidproof brick.

Tanks where brine is treated for precipitation of soluble magnesium and calcium sulphates are usually plain steel or rubber- or brick-lined steel. It is reported that a German plant filtered the resultant slurry through polyvinyl cloth on wooden frames, while another filtered brine on its way to cell feed tanks through a paper medium. The paper had been in use since cotton became critical and had proved to be more satisfactory than cotton both in longer life and lower turbidity of the brine.

The temperature of the purified brine is raised in steel heat exchangers, and the solution saturated with salt. It is then reheated to prevent salt precipitation in the distribution mains. The warm saturated brine goes to the cell through hard-rubber lines and enters the cells through tantalum orifices.

In the case of the diaphragm cells, steel tanks with concrete or soapstone covers are used. To reduce the weight of covers, asbestos fibers can be added to the mix. Steel is used in the form of wire-mesh screen on perforated sheet for the cathode. The anode is graphite treated with linseed oil or other impregnating material. In mercury cells, rubber-lined steel tanks are used. Most of the bottom is left unlined so that the electric contact with the mercury cathode can be established. The cover is rubber-lined steel, although sandstone was formerly employed. Natural rubber is said to have a longer life than GR-S.

Warm moist chlorine from the cells is usually led through chemical-stoneware pipe to rubber-lined mains. The rubber is reported to have a life of 5 years. It is cooled in a stoneware, glass-lined, or rubber- and brick-lined steel heat exchanger. The gas leaves the exchanger in stoneware lines.

Removal of the moisture is necessary. This is done in stoneware or acid-resistant-brick drying towers by allowing sulphuric acid to come into contact with the gas in countercurrent flow. After drying, the gas passes through steel pipe lines, traps, and condensers to steel storage tanks. It can be handled in cast-iron pumps and compressors. High-silicon pumps are used whenever sulphuric acid is present.

HCl Hydrolysis Process.—Members of the U.S. Chlorine Industry team investigated an I.G. Farbenindustrie electrolytic process for the recovery of chlorine from by-product hydrochloric acid at Wolfen in May, 1946. (Gardiner, W. C., Hydrochloric Acid Electrolysis, *Chem. Eng.*, Vol. 54, No. 1, p. 100, 1947.) The cell had been recovering about a ton of chlorine per day.

It was a series-type cell with bipolar graphite electrodes built like a filter press. It had 30 units, each unit operating at about 2.3 volts at 1,000 amp. A novel feature of the cell was that broken pieces of scrap graphite actually formed the anode and were gradually consumed but readily replenished. The Wolfen cell had a total voltage of about 70 volts, but the construction was such that it could be built for higher voltages. It had been operated up to 1,500 amp.

Concentrated acid from an absorber was circulated through the cell and removed as approximately 10 per cent acid, which was returned to the absorber for resaturation.

Essentially the cell consisted of an anodic end section, a cathodic end section, and an intermediate section plus supporting and clamping equipment. The concentrated hydrochloric acid entered at the bottom on one side of the anodic end section and was distributed by a canal formed by holes in adjoining sections. Near the top, similar canals served to draw off chlorine on one side and hydrogen and hydrochloric acid on the other.

Each intermediate section or unit cell had an outer frame of insulating material into which graphite slabs were cemented. The graphite was smooth on the anodic side and ribbed on the cathodic side. A polyvinyl chloride cloth diaphragm was cemented across one face of the frame, touching the cathodic graphite ribs. The space between the anode of one section and the diaphragm of another was filled with scrap graphite about 15 mm. in size. The graphite and the diaphragm were impregnated above the liquid level with a polyvinyl chloride lacquer in order to prevent diffusion and mixing of the liberated gases. A gasket of soft polyvinyl chloride with perforations for the various canals was used between frames.

The frames for the end sections were thicker. The canals were closed on the end but opened on the side for pipe connections. Graphite blocks with ribs were cemented into the cathodic end section and also the diaphragm, while the anodic end section had plain graphite slabs with a cavity for the broken graphite and filling holes on the top side.

Electrical connections were made to each end piece by ten round copper rods 50 mm. in diameter by 145 mm. long screwed into the graphite 70 mm. The contact holes were probably impregnated with linseed oil.

The press for clamping the sections together rested on two rubber-covered 4-in. I beams supported on porcelain insulators. The cell was surrounded by a curb, and the floor and curb were coated with an acid-resistant cement.

When the cell was operated with 32 per cent acid in the feed and 10 per cent acid out, the voltage was 2.3 volts per unit at 1,000 amp. and the current efficiency was 92 to 94 per cent. The cell temperature was about 80°C. The acid flowed into the anode compartment, up through the broken graphite, and then through the diaphragm into the cathode compartment and out. Some dissolved chlorine was thus carried into the cathode compartment accounting for some of the inefficiency, while current leakage represented the rest.

Both the Cl_2 and H_2 were scrubbed with water to remove HCl. After washing, the anode gas was 99.9 per cent $Cl_2 + CO_2$ of which 0.2 to 0.4 per cent was CO_2.

The broken graphite was consumed, whereas there was no attack on the graphite plates. Every 3 months more graphite was added through the holes in the top of each frame. The fine graphite was normally consumed, but under certain circumstances, such as low-acid concentration, an excess of fines was formed, which caused a bridging effect at the top of the compartment. Some means of periodically flushing out the fines would have been desirable but had not been developed. The consumption of graphite was 0.9 lb. per ton of chlorine. Scrap graphite from Billiter cell anodes was used.

After 14 months of operation the diaphragm was as good as new. The Haveg frames showed some spalling and efflorescence but would be satisfactory for a long time. However, the operators thought that rubber-covered steel would be better. Organic and sulphur compounds were present in the hydrochloric acid but apparently gave little trouble. It was thought that it might be necessary to treat the acid with activated carbon in some cases.

Handling

Dry Chlorine.—Extra-strong black-iron or steel pipe is recommended for dry chlorine or gaseous chlorine, although copper and other materials that will withstand high pressure and chlorine can be used. Steel, cast iron, wrought iron, most copper alloys, most nickel alloys, certain stainless steel, and lead are common materials for mechanical construction. (Pittsburgh Plate Glass Co., Columbia Chemical Division, "Chlorine," 1948.)

Gaskets should be made of asbestos composition or lead containing 3 per cent antimony. Rubber gaskets should never be used on liquid-chlorine lines.

Drop forged-steel globe or needle valves of a type specifically designed for liquid-chlorine service are recommended. Valves with special brass or nickel alloys of sturdy design can also be used. In general, valves in chlorine service should embody a sturdy design, employ Monel or Hastelloy C trim, and have a deep packing recess containing braided graphitized asbestos rope or special preformed rings made of rubber-impregnated cotton cord lubricated with beeswax and graphite.

Pressure gages, protected by a silver or tantalum diaphragm, are the only type recommended.

Flexible, annealed-copper tubing of 500 lb. working pressure, in the form of a loop or S bend, is recommended for making connections to chlorine cylinders, ton tanks, and tank cars. Copper tubing becomes hard and rigid after continued use and should be replaced.

Wet Chlorine.—This is very corrosive to all the common construction metals. At low pressures, wet chlorine can be handled in chemical stoneware, glass, or porcelain equipment and by certain special alloys and plastic compositions. The noble metals gold, platinum, and silver are resistant, as is tantalum, which is totally inert to both wet or dry chlorine at temperatures below 300°F. For higher pressures, combinations using resistant lining materials with the common metals for strength are employed.

Lead.—Lead is recommended as a material for handling moist chlorine up to 230°F. with slight corrosion, and the chemical when dry has very little effect on lead. Small amounts of chlorine, such as are used in water treatment, have no effect on lead. When chlorine with some moisture present results in the formation of small amounts of dilute hydrochloric acid, there is a possibility of slight corrosion, depending on the amount and upon other conditions.

Chlorine is a gas at room temperature and is inert to most metals when cool and dry, but the dry gas when heated attacks all metals to a certain extent. Hydrochloric and hypochlorous acids, formed in the presence of moisture, attack most metals except platinum, silver, lead, and certain special alloys. A protective layer of lead chloride forms over the lead, and further corrosion is resisted, while the film remains intact. This protective film permits the use of lead with moist chlorine up to 230°F. with only slight corrosion.

Pure lead tubing gives satisfactory length of service without undue expense. In general, at room temperature, corrosion of lead by wet or dry chlorine, either liquid or gaseous, is sufficiently moderate to recommend the use of lead from an economic standpoint. (Church, H. M., Lead, *Chem. Eng.*, Vol. 54, No. 1, p. 211, 1947.)

High-silicon Irons.—High-silicon irons have long been familiar to the chemical industry as materials of construction where resistance to corrosion is a prime consideration. Both of the common analyses, *i.e.*, Si, 14.5; Mn, 0.75; C, 0.90 max., and with or without 3 per cent Mo, have been found satisfactory for certain applications in the handling of chlorine gas, wet and dry, and chlorine water.

Handling of dry chlorine gas presents no particular problem from the standpoint of corrosion, as it is inert to most metals and alloys, including the high-silicon irons. (Traub, J. L., High-Silicon Irons, *Chem. Eng.*, Vol. 54, No. 1, p. 211, 1947.)

Chemical Porcelain and Stoneware.—Because of their remarkable chemical stability, they find great usage in the presence of chlorine and chlorine in combination with a great variety of other chemicals. For example, in the electrolytic manufacture of chlorine gas, porcelain and stoneware piping and valves are used for conveying the wet gas from the cells. Chemical-porcelain and stoneware towers are used for drying the chlorine gas in the presence of concentrated sulphuric acid before the chlorine is liquefied.

In the process industries where chlorine gas is present in conjunction with other chemicals in minute or large quantities, the universal chemical stability of these materials is of great value. In a typical chlorination reaction, porcelain or stoneware equipment can be used for conveying the individual chemicals entering the reaction and handling gases, waste products, and the finished product. It is apparent that the broad stability of these materials in the presence of wet chlorine, mineral acids, and chlorine compounds makes them versatile materials of construction for the process industries.

Chemical-porcelain equipment used in handling chlorine gas includes metallic flanged pipe, pipe fittings, plug cocks, angle valves, Y valves, safety valves, tower packings, and a great variety of special equipment. (Chowning, J. S., Chemical Porcelain, *Chem. Eng.*, Vol. 54, No. 1, p. 214, 1947.)

Vitreous Silica.—In general, vitreous silica is not attacked appreciably by chlorine in the absence of other materials at temperatures below 1650°F. The presence of carbon, however, appreciably increases the degree of attack. (Quinn, R. J., *Chem. Ind.*, Vol. 51, No. 6, pp. 872–876, 1942.) Fused silica is suitable for handling chlorine at high temperatures and is the only material except platinum that can be used for this purpose.

Worthite.—Worthite is definitely not suitable for contact with wet chlorine gas. Dry chlorine gas at normal temperatures does not attack Worthite, but since steel is suitable for handling dry chlorine gas as well as the liquid, there is no economical application for Worthite in these environments. (Pratt, W. E., Worthite, *Chem. Eng.*, Vol. 54, No. 2, p. 219, 1947.)

Tantalum.—Tantalum has been found inert to chlorine gas, either dry or wet, at all temperatures up to 300°F. and to chlorine water. One of the first uses of tantalum was in diaphragms and needle valves for proportioning the flow of chlorine into municipal water supplies. It is still used extensively for this purpose.

Tantalum heat exchangers have been used since 1935 for reacting chlorine with ammonia to produce chemically pure ammonium chloride. Tantalum heaters and condensers are used in numerous other applications where either chlorine or chlorides present a corrosion or contamination problem. (Scribner, L. R., Tantalum, *Chem. Eng.*, Vol. 54, No. 2, p. 219, 1947.)

Silicones.—In one industrial application, gaskets of Silastic 180 are used to seal the connection between a glass pipe and a ceramic elbow in a line carrying steam at 220°F. and a 90 to 95 per cent concentration of wet chlorine gas. In this service, black rubber gaskets hardened and started to leak after 2 or 3 days. Gaskets of Silastic 180 are still flexible enough to give a tight seal after 6 weeks of service. (McHard, J. A., Silicones, *Chem. Eng.*, Vol. 54, No. 2, p. 219, 1947.)

Rubber Lining.—Rubber-lined tanks, pipes, and fittings, using both natural and synthetic rubbers, have been widely used in industrial installations involving wet and dry chlorine gas and chlorine water.

The dry gas has very little effect on rubber linings. Wet gas, on the other hand, does react with the surface to form a skin of rubber chloride. Chlorine water reacts the same as the wet gas—the extent of the reactions, of course, being dependent upon the concentration of the solution. The character of this reacted surface and the depth to which the reaction occurs can be controlled by specific compounding of the rubber. Soft-rubber vulcanizates react most readily and tend to form a skin of chloride which is brittle and quite strongly adheres to the unreacted rubber beneath. Semihard and hard rubber react more slowly and to a lesser depth than the soft rubbers; however, the chlorinated surface tends to powder off more readily. In services involving abrasion, these hard products are sometimes subject to more rapid disintegration than soft rubber for the reason that the reacted surface is readily abraded away, thus exposing more unreacted rubber.

In such cases, soft rubber is preferred despite its greater susceptibility to chlorination. The reason, as noted above, is that the reacted surface is more resistant to abrasion and is firmly anchored to its parent material.

In the majority of industrial services involving chlorine, abrasion is not a factor and semihard or hard rubbers are best suited. The initial reaction is rapid, but the surface-reaction product forms a protective film which inhibits further attack. (True, O. S., Rubber Lining, *Chem. Eng.*, Vol. 54, No. 2, p. 222, 1947.)

Carbon and Graphite.—Carbon, graphite, and Karbate-brand impervious carbon and graphite are unattacked by dry chlorine. Carbon and graphite are used in reactors employing dry chlorine at temperatures ranging as high as

3000°F. with no measurable attack. Such applications involve linings, tubes, heating elements, crucibles, porous carbon and perforated diffusers, and a variety of special parts.

With the exception of avoiding strong oxidants (at the specific temperatures involved), there are apparently no limits on gas concentration, temperature, or contaminants. For example, any mixture of chlorine and air can be used up to the temperatures at which carbon and graphite are subject to oxidation in air, *i.e.*, 625 and 800°F., respectively.

The corrosion characteristics of Karbate are similar to those of carbon and graphite, with the exception that the maximum operating temperature of the material is limited to 340°F. This material is used extensively in systems involving the chlorination of hydrocarbons. It is especially valuable in those reactions where hydrogen chloride is a by-product, since it is equally inert in chlorine and hydrochloric acid at all concentrations. Diffusers, heating or cooling elements, condensers, piping, valves, pumps, and by-product hydrochloric acid systems are regularly used in connection with the chlorination of alcohols, acetic acid, and aliphatic or aromatic hydrocarbons. (Werking, L. C., Carbon and Graphite, *Chem. Eng.*, Vol. 54, No. 2, p. 226, 1947.)

Hastelloy.—One alloy that does possess the necessary corrosion resistance and physical properties for handling wet chlorine gas is Hastelloy C. Under some conditions Hastelloy C has shown up very favorably in handling chlorine gas at temperatures as high as 1800°F., where, of course, very little moisture is present.

Hastelloy C has been successfully and extensively employed for handling chlorine, both wet and dry, in such equipment as valves, piping, vessels, cracking tubes, and feed pipes. It is used in one form or another for chlorinating equipment used for water purification. Chlorinating tubes for bubbling chlorine into sodium hydroxide to produce bleaching agents are outstanding applications for this alloy. One precaution, however, should be mentioned here in connection with this type of service. In a few instances where the stronger bleaching compound has been used, the alloy has tended to catalyze the sodium hypochlorite, causing decomposition of the sodium hypochlorite solution. Although this condition has occurred in only three out of several hundred installations, it is suggested that this possible situation be checked before using Hastelloy for this service. Decomposition seems to occur only in the very strong bleach solutions containing 15 to 18 per cent free chlorine. (Chisholm, C. G., Hastelloy, *Chem. Eng.*, Vol. 54, No. 2, p. 228, 1947.)

Wood.—In many industries where wet and dry chlorine gas and chlorine water are used, wood tanks are used in the process, and available records show that some tanks have been in constant use for over 40 years.

One of the largest users of chlorine and of wood tanks is the pulp and paper industry. Chlorine is used in connection with the direct bleaching of the pulp, as a deodorant for sulphate pulp, and sometimes for algae and slime control. A survey of pulp and paper mills disclosed that wood tanks have been highly satisfactory in these services. (Chaney, S. E., Wood Tanks, *Chem. Eng.*, Vol. 54, No. 2, p. 232, 1947.)

Durimet.—Durimet T and Durimet 20 have been used for chlorine gas, wet and dry. The lower cost of the high-silicon irons and their generally more satisfactory life have limited the use of Durimet in the services under consideration. It has been used where machinable alloys are required and metals preferred to other materials.

Neither of the Durimets is recommended for wet chlorine gas or chlorine water at elevated temperatures without prior testing under operating conditions. One authority, however, has reported Durimet as being satisfactory in moist chlorine at temperatures up to 800°F. (Traub, J. L., Durimet and Chlorimet, *Chem. Eng.*, Vol. 54, No. 3, p. 213, 1947.)

Nickel Alloys.—Nickel, Monel, and Inconel are resistant to dry chlorine even at considerably elevated temperatures. At high temperatures they are among the most resistant materials. Experience has shown that the useful upper temperature limit for nickel and Inconel is 1000°F. and for Monel about 850°F. This resistance also extends to wet chlorine gas as long as the temperature is always well above the dew point of the chlorine-water vapor mixture.

Ni-Resist is also resistant to dry chlorine at atmospheric temperatures. The upper temperatures for its use are about 400°F. for Type 1 Ni-Resist (Ni, 14; Cu, 6) and about 450°F. for Type 3 Ni-Resist (Ni, 30).

Monel is a standard material for trim on chlorine cylinder and tank-car valves and for orifice plates in chlorine pipe lines. It is used frequently for parts of chlorine-dispensing equipment. Common applications of Monel and nickel are for reactors, agitators, heating coils, valves, piping, and other parts in connection with the chlorination of organic materials where the reactants are essentially water-free.

None of these materials is resistant to wet chlorine at temperatures below the dew point of the chlorine-water mixture or in continuous exposure to chlorinated water solutions except in very dilute chlorine concentrations. (Friend, W. Z., Nickel, Nickel Alloys, *Chem. Eng.*, Vol. 54, No. 3, p. 213, 1947.)

Chemical Stoneware.—This material is largely used in the production of chlorine by the electrolytic process. It withstands hot wet chlorine in these applications. The same properties which make chemical stoneware so well adapted for manufacturing purposes also make it suitable for the usual handling applications, which include absorption and reaction towers, ducts and exhausters for either concentrated gas or fumes, reactors (limited by size and pressure), and piping, fittings, and pumps for handling chlorine water. Stoneware is not generally used for dry chlorine, as more economical materials can be used. (Herstein, F. E., Chemical Stoneware, *Chem. Eng.*, Vol. 54, No. 3, p. 216, 1947.)

Haveg.—From a corrosion standpoint, Haveg is recommended for chlorine, wet or dry, as well as for chlorine water. Haveg in the form of duct work and cell headers has been in continuous service for 15 years without attack. For normal chlorine service, either pure or with traces of hydrochloric acid or other inorganic impurities, Haveg 41 or Haveg 60 gives excellent service. Where chlorine is to be used in the presence of organic solvents such as benzene, ethylene dichloride, alcohols, or chloracetic acid Haveg 60 is recommended. Over a wide range of chlorine handling, both in production and reaction with other chemicals, Haveg will give an installation that is entirely permanent. (Gayle, D. R., Haveg, *Chem. Eng.*, Vol. 54, No. 5, p. 244, 1947.)

Glass-lined Steel.—It is used very extensively for wet chlorinations, at elevated temperatures and pressures, and in the presence of other corrosives such as hydrochloric acid and organic acids, as reactors, piping, condensers, etc.

Stainless Steel.—Although chlorine is one of the most corrosive substances known, stainless steel offers useful resistance to attack in applications including tubing for carrying dry chlorine gas, tanks, pipe lines, screens, and pump parts for handling certain bleaching solutions and rinse waters in pulp- and textile-bleaching processes, sterilizing equipment, and other services where the operating conditions are properly controlled.

Types 304, 316, and 317 are suitable for exposure to dry chlorine gas and to mixtures of dry air and chlorine gas at low temperatures. If moisture is present, rapid attack will occur at all temperatures owing to the formation and condensation of hydrochloric acid. Severe attack can be expected when the dry gas is used in the vicinity of 800 or 900°F.

Most of the industrial pulp- and textile-bleaching applications involve solutions of unstable chlorine compounds such as the hypochlorites, which decompose rapidly to form free chlorine and chlorides. Type 304 offers excellent resistance to corrosion in calcium hypochlorite solutions containing up to 3 per cent available chlorine for periods of exposure not exceeding 4 hr. The metal must be rinsed thoroughly with water immediately after use. Types 316 and 317, which are more resistant than Type 304 to attack by pitting, are the best grades for exposure to solutions of this kind. They have been used successfully for handling alkaline sodium hypochlorite solutions containing 0.3 per cent available chlorine in equipment for entire bleaching cycles.

Protective Coatings.—Resistance of most organic materials to chlorine, wet or dry, is usually rather poor. The baked phenol-formaldehyde resins are not recommended. The vinyl resins have been used to some extent up to 100°F. Amercoat No. 33 has been used in the manufacture of calcium and sodium hypochlorite solutions. Prufcoat has been used as the protective coating over concrete in sodium hypochlorite solutions. For low residual amounts of chlorine in potable water, Prufcoat has been successfully used on some occasions.

Tygon paint is reported to be giving splendid service in exhaust systems as a protective coating for fans and ducts handling chlorine. The user, however, finds that this type of paint is difficult to apply. Bakelite varnish is reported as almost as good and many times easier to use.

Steel piping around the chlorine plant of Basic Magnesium Co. was coated with a bituminous covering to protect it.

The bleach plants of the pulp and paper industry were extensive users of chlorinated rubber-base paints on equipment and structural members before the war and found them highly satisfactory.

Saran.—Saran-lined pipe has been successfully used for wet chlorine for bleaching oils from fats. It has been used also for introducing dry chlorine under pressure at the bottom of a tank of dilute caustic soda. Among the other uses to which Saran-lined pipe has been put are (1) introducing wet chlorine into solvents, (2) chlorinated hydrocarbons, (3) in connection with a chlorine bath.

Packaging

Dry chlorine can be shipped in welded-steel cylinders, single-unit tank cars, multiunit tank cars, or other containers.

CHLORINE—SULPHURIC ACID

Both Chlorimet 2 and 3 proved highly resistant to a 56°Bé. sulphuric acid solution saturated with chlorine gas. (Luce, W. A., Chlorimets, *Chem. Eng.*, Vol. 55, No. 8, p. 224, 1948.)

CHLORINE DIOXIDE

Chlorine dioxide is a powerful oxidizing and bleaching agent but because of its instability it cannot be produced in bulk and stored. In order to apply it for any purpose, it must be generated in very low concentration at the point of use. (Woodward, E. R., G. A. Petroe, and G. P. Vincent, New Process for Producing Chlorine Dioxide for Industrial Use, *Trans. A.I.Ch.E.*, Vol. 40, pp. 271–290, 1944.)

Production

Materials of Construction.—Several processes are used to generate chlorine dioxide for bleaching flour and for other purposes. In each case the materials of construction vary to some extent.

When it is made by treating dry sodium chlorite with chlorine, the generators consist of steel towers lined with chemical stoneware or glass. To guard against hazards, the towers are mounted over apertures in a boxlike sheet-steel base and each tower is closed at the bottóm with a thin silver safety disk. The chlorine filters are glass pipe packed with silica gel.

All chlorine-carrying parts of the system are made of noncorroding materials such as silver, Hastelloy C, glass, and plastics. Silver is used for the high-pressure tubing, and the plastic compound Saran for the low-pressure tubing. The use of iron is avoided as much as possible in order to reduce the formation of a gummy substance, composed largely of ferric chloride, that tends to clog up piping, valves, and other parts of the equipment.

Chlorine dioxide formed in the generator, highly diluted with air, is led through Saran tubing.

When the chlorine dioxide is made by the Griesheim process, the generators are made from stoneware and from iron lined with polyvinyl chloride protective coating and are equipped with cooling coils of Heschotherm, which is a silicon carbide ceramic material with high heat-transfer coefficient. (Griesheim, Chlorine Dioxide and Sodium Chlorite at I.G. Farben., FIAT Final Report 825, British Intelligence Objectives Sub-Committee, His Majesty's Stationery Office, London.)

Chlorine—Dry Chlorite Process.—Two steel towers are filled with sodium chlorite. A mixture of chlorine and a large excess of air is fed into the bottom of one tower. Chlorine dioxide, formed in the tower, is carried out at the top. The ClO_2 then enters the base of the second tower and passes out at the top into the mixed-gas manifold. The operation takes place at room temperature. (Woodward, *loc. cit.*)

Griesheim Process.—Sodium chlorite was produced according to two methods, and in both cases ClO_2 was produced by introducing a mixture of SO_2 and air in a mixture of sodium chlorate and sulphuric acid. In one case the chlorine dioxide was absorbed in NaOH and H_2O_2, whereas in the second case fine zinc dust suspended in water was used as the reducing agent which formed the difficultly soluble zinc chloride with the chlorine dioxide.

CHLOROBROMOMETHANE

Dry chlorobromomethane (maximum water content 0.02 per cent) is practically noncorrosive to steel, brass, and lead. This is important, since these metals are commonly used in fire extinguishers, and attention is being given to the use of this chemical as an extinguishing agent. It is corrosive, like most halogenated hydrocarbons, on aluminum, magnesium, and zinc, attacking such metals rapidly. (Anon., Chlorobromomethane, *Quart. Natl. Fire Protect. Assoc.*, Vol. 42, No. 1, pp. 46–50, 1948.)

CHLOROTOLUENE-SULPHONIC ACID

After the war a British team of investigators found that the German I.G. Farben. had been producing 4-chlorotoluene-2-sulphonic acid. (Adams, D. A. W., and W. Baird, Some Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.) This acid was made at the Leverkusen plant by the Sandmeyer reaction on the corresponding toluidine sulphonic acid.

Production

Materials of Construction.—Nonmetallic materials are used for the equipment. The diazo compound is sensitive to the presence of iron and lead. The metals must be absent from the plant. Mixtures of cuprous chloride and hydrochloric acid attack lead strongly, and materials of construction should be rubber-lined with a further tile lining or glass-lined steel.

Process.—Water, 4-aminotoluene-2-sulphonic acid, and crude hydrochloric acid (19.5°Bé.) are charged to a brine-cooled enameled pan provided with a stirrer. The mixture is stirred and cooled to -10 to -15°C. If necessary, the sulphonic acid and hydrochloric acid are ball-milled in a rubber-lined mill. The suspension is diazotized by addition of 30 per cent sodium nitrite solution, the temperature being allowed to rise to 10 to 15°C. The diazotization is continued until a strongly diluted sample shows presence of free nitrite. At this stage the liquor is of a light color, the diazo being relatively insoluble.

It is convenient to make up sufficient cuprous chloride solution for several batches of diazo. This is done as follows:

Crude hydrochloric acid and copper are charged to a tiled vessel with a rubber undercoating, provided with a rubber-covered gate stirrer, blow leg, and earthenware cocks, etc. When the copper is charged to the acid, the temperature rises to about 50°C. and the batch is stirred to effect solution, after which insoluble material is settled out and the cuprous chloride estimated by titration with permanganate.

A kettle is used for the Sandmeyer stage. It is rubber-lined with two layers of tile on top. The paddle stirrer is also rubber-covered. The pan is charged with cuprous chloride solution and filled with 19.5°Bé. hydrochloric acid. Open steam is passed in to raise the temperature to 75°C. Then the diazo is added. The evolved gases pass by a rubber-lined pipe to a chimney. When the decomposition is complete, a further 30 per cent nitrite solution is added to diazotize any unreacted base. A sample coupled with naphtholsulphonic acid in sodium carbonate solution should give no dyestuff formation; further amounts of nitrite are added if necessary to achieve this.

The batch is now cooled to 15 to 20°C. preferably by applying vacuum with a rubber-lined steam ejector to distil off water. Then 12 per cent of salt, based on the volume of the batch, is added, and after stirring, the product is filtered. The nutsche cake is first washed with saturated salt solution to remove copper and then with water to remove salt. The copper-containing salt liquor should not contain any product capable of being salted out and is sent for copper recovery. The water wash liquor is used in making up the brine for the next brine wash.

CHROMIC ACID

Chromic acid forms immediately when chromium trioxide is dissolved in water.

Production

Materials of Construction.—There is no particular problem in making the chromium trioxide. Plain iron and steel are used. However, conversion to chromic acid causes corrosion as does the handling of the acid. Experience in one United States plant showed plain steel and also Type 316 stainless to be poor as materials of construction. Nor is high-silicon applicable to this use.

Process.—At Leverkusen, the I.G. Farben. made the trioxide by feeding together sodium bichromate crystals with 96 per cent sulphuric acid into a circular steel tank fitted with an agitator in the proportion of 420 kg. of the crystals to 304 kg. of acid. When the required quantities of acid and crystals are thoroughly mixed together, gas heating is applied to raise the temperature of the mixture to 200°C. At this temperature the reaction takes place, the molten mass separating into two distinct layers, the upper being sodium bisulphate and the lower chromic acid. (Hutton-Wilson, M. J. C., and G. M. Hay, British Intelligence Objectives Sub-Committee, His Majesty's Stationery Office, London.)

The chromium trioxide is drawn off into cast-iron pans, where it is allowed to solidify before being crushed and packed for sale.

Handling

Since chromates form a good protective coating on lead, it can be used with fairly high concentrations of chromic acid. The use of a lead alloy containing 7 per cent tin for handling chromic acid solutions at both low and high temperatures is on the increase.

Illium has been reported as satisfactory for use in pumps handling 1½ to 36 per cent acid at 70°F. High-alloy stainless steels such as Worthite and Durimet 20 are resistant at all concentrations and temperatures but should not be used in equipment for dissolving chromic acid crystals. Dilute solutions can be handled by stainless-steel pumps. Glass tanks are in use. Vinyl copolymer protective coatings are satisfactory for some applications. A chemical firm making very pure chemicals uses glass-lined and stainless-steel equipment.

Another company uses lignum vitae spools as retainers of glass panels in a 10 per cent chromic acid solution. The wooden spools replaced laminated phenolic resins, which were more expensive and more difficult to machine. The lignum vitae is not submerged in the acid but is exposed to acid vapors and occasional acid washes. (Callaham, J. R., Lignum-Vitae Wood for Processing Applications, *Chem. & Met. Eng.*, Vol. 51, No. 5, pp. 129–131, 1944.)

High-silicon iron is highly resistant to pure and crude chromic acid at all temperatures and concentrations. This alloy is extensively used in the plating industry for pumps, valves, heat exchangers, pipe lines, tank outlets, etc., where chromic acid is handled.

For chrome-plating tanks a specially developed, high-grade iron-free chemical-stoneware slab or tile set in a special type of acidproof cement is now used. (Rauh, C. A., Pyroflex Constructions for Acid and Alkali Service, *Trans. A.I.Ch.E.*, Vol. 35, p. 471, 1939.) Before lining is applied, Pyroflex strips are fused over all welds permanently to block off the acid from these areas, which represent the only weak spot in the outer steel shell in so far as corrosion is concerned. This type of construction is now frequently used in chrome-plating tanks.

An engineer in a plant making chromic acid reports that he has never been able to solve the problem of finding a material that will stand up in his acid flakers. Under the double action of corrosion and abrasion, the rolls corrode and form pits in which the flakes stick. When pressure is put on the knives to scrape out the pits, the knives are ruined.

He used a high-carbon steel, but the chromic acid seemed to take the carbon out of the steel and even went to work on the steel in some places. He tried chrome plate, but the hot acid loosened it. Then he went to the use of an extra-heavy steel and found it necessary to resurface the rollers about once every 8 months.

Packaging

Steel drums are in use for shipment of chromic acid.

CHROMIC ACID—SODIUM BISULPHATE

A chemical plant has occasion to handle a solution consisting of chromic acid (2 to 100 per cent) mixed with sodium bisulphate (1 per cent to saturated solution) at temperatures up to 150°F. High-alloy stainless steels such as Worthite and Durimet are reported to be used exclusively for pump and valve parts. Lead and 18-8 stainless steel are also satisfactory and are used for those parts of the equipment which are not produced as castings. Although 18-8 stainless is satisfactory here, where at least 2 per cent chromic acid is present to act as an inhibitor, the plant engineers are certain that it would not be satisfactory in the presence of sodium bisulphate alone.

CITRIC ACID

Citric acid occurs in certain fruit from which it is recovered. It is made also from sucrose by fermentation. The latter source is now the more important from a volume standpoint.

Production

Materials of Construction.—Equipment used for recovery of citric acid from lemons and other citrus fruit is made up of many materials of construction. The juice-extractor rolls may be bronze (zinc-free), nickel, or stainless steel. The fermenting tanks are wood. Filter presses for the juice are wood, bronze, nickel, or stainless steel. Neutralizing tanks are wood. Calcium citrate filters are bronze or nickel-lined steel. Citric acid filters are lead-lined steel. Crystallizing vats are wood- or lead-lined steel. Vacuum pans for purification are cast lead or steel, lead-lined steel, or 18-8 S-Mo steel. Recrystallization tanks are stoneware, wood, Monel, nickel-lined steel, or block tin. Decomposing tanks are made of cast lead or lead-lined steel. (Anon., *Chem. & Met. Eng.*, Vol. 41, No. 10, Supplement, 1934.)

A Monel chamber is used for spray drying of citric acid. Monel evaporators are used for concentration of citrus juices. Nickel and Inconel heating coils are used in juice pasteurizers.

Citric acid is processed in considerable quantity for pharmaceutical and food use. Because of very low U.S.P. limits on lead content, there has been a trend throughout the industry to get away from lead equipment in processing these materials. (Corrosion Reporter, *Chem. & Met. Eng.*, Vol. 52, No. 10, p. 211, 1945.) This plant has completely replaced lead in favor of stainless steel or Monel. Type 316 stainless is preferred to Type 304, though the latter will do if need be. In a reducing environment or in the presence of sulphides, Type 316 stainless steel is preferable to Monel.

Otherwise, stainless steel and Monel are more or less interchangeable and are used for all customary equipment such as reaction vessels, agitators, pipe lines, and pumps. These handle any concentration of the acid and at any temperature up to about 120°C. How the alloys would perform at higher temperatures has never been demonstrated, since there has never been occasion to exceed 120°.

Process Based on Fruit.—Off-color or -size fruit such as lemons, oranges, limes, and grapefruit is generally used as raw material. The fruit is pressed, and the juice filtered. It is then treated with lime to form calcium citrate, which is subsequently treated with sulphuric acid to regenerate the citric acid. The dilute citric acid is then evaporated and crystallized.

Synthetic Process.—This process is based on the fermentation of sucrose by a strain of *aspergillus niger.* (Shreve, R. N., "The Chemical Process Industries," 1st ed., p. 672, McGraw-Hill Book Company, Inc., New York, 1945.) Although no information has been published, apparently this process is an aerobic one, the mold flourishing as a surface mycelium on the sugar solution, held in shallow pure aluminum trays for probably less than 9 days. The microorganism effects an oxidation to citric acid. Although some of the sugar is utilized by the organism's respiratory activity, being converted to CO_2 and other products, the yields are good.

Handling

Aluminum is used in both the production and handling of citric acid because of the fact that any slight contamination with aluminum salts is not objectionable in the use of the acid in beverages.

High-alloy stainless steel such as Durimet or Worthite equipment is in plant service for handling solutions of citric acid. Plate-and-frame press, valves, and fittings and open impeller centrifugal pumps are used on a citric acid product.

Wood is used for storage tanks. Copper or bronze equipment can be used to handle this acid. Aqueous solutions are being handled by all-bronze or stainless-steel pumps. Karbate can be used to handle all concentrations up to boiling. Copper is used for filters and piping. Phenolic and vinyl copolymer protective coatings are satisfactory.

Packaging

Wood barrels or wooden boxes are used for small quantities; glass bottles for a few pounds. In some cases paper containers are used. Containers are lined with moistureproof materials.

CITRIC ACID—SULPHURIC ACID

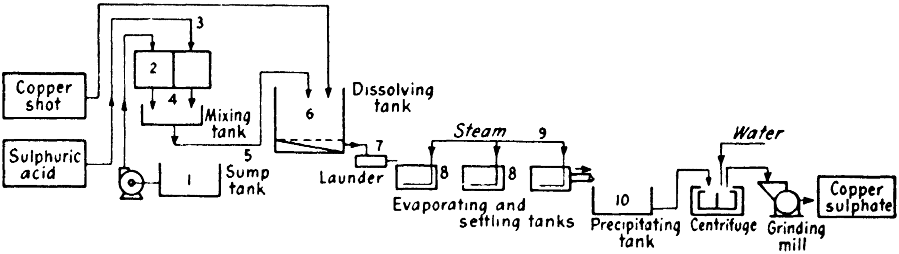
Sulphuric acid is commonly involved in certain citric acid treatments. The combination of these two acids is exceedingly corrosive. Durimet 20 can be used for pumps, valves, etc., in this service. Extensive tests conducted on the problem indicated that even the high-silicon iron alloys would contaminate this corrosive mixture sufficiently to preclude their use. (Luce, W. A., Corrosion Problems in the Food Industry, *Anglo-American Industrial Newsletter,* February, 1948.)

COPPER SULPHATE

Copper sulphate, or blue vitriol as it is commonly called, is produced in this country principally as a by-product of electrolytic copper refining, although it is also produced by leaching metallic copper with dilute sulphuric acid.

Production

Materials of Construction.—Creosoted cypress wood, lead-lined wherever necessary, is probably the single most important requirement in copper sulphate production. Acidproof concrete is also effectively used. Wrought iron, too, has a very favorable record of experience in applications that do not involve severe corrosion problems. (Barker, P., Copper Sulphate, *Chem. & Met. Eng.*, Vol. 41, No. 10, p. 520, 1934.)



Copper sulphate.

1. Steel
2. Steel
3. Steel
4. Lead-lined wood
5. Lead, lead-lined steel
6. Lead-lined wood, lead false bottom
7. Lead-lined wood
8. Lead-lined wood
9. Wrought iron or steel
10. Lead-lined wood
11. Copper basket
12. Manganese steel

The dissolving tank is circular. Six triangular-shaped pieces of wood are placed upon the bottom, and a false bottom is nailed on. The whole tank is then lined with sheet lead. Six triangular pieces of wood are placed on the false bottom, so that the channels between lead to the overflow; seven lead-covered strips are placed upon these to support the perforated bottom, which is made of lead. Upon the perforated bottom, a lead pipe for steam is laid, which is allowed to exhaust inside the tank. (Barker, P., Blue Vitriol Produced by Leaching Shot, *Chem. & Met. Eng.*, Vol. 39, No. 5, pp. 258–261, 1932.)

Settling and precipitating tanks are made from wooden boards lined on the sides and bottom with lead. If the wooden tanks are painted inside and out previous to lining with three coats of acidproof paint, they will last 10 years.

Acid lines are lead, lead-lined steel or ordinary steel in the case of concentrated acid. Steam lines are wrought iron or ordinary steel. Centrifuges have copper baskets reinforced with copper rings. The grinding equipment includes manganese steel in rolls and hammer mills and flint balls in ball mills.

Copper and H_2SO_4 Process.—Copper must be in the form of shot in order to provide maximum surface for oxidation and solution. Oxidation and solution of the copper take place in a lead-lined dissolving tank. Sulphuric acid mixture is sprayed over the shot. The mixture is led to the center cup through the lead feed pipe and escapes through radial perforated pipes. Live steam is forced in through injectors. The shot is heated to 180 to 200°F.

The spray is stopped at the end of the day's operation, and the mother-liquor–sulphuric acid mixture is dried on the shot by the heat, forming a coating of copper oxide and some sulphate. After the drying of the salts on the shot has progressed sufficiently, the mother-liquor–sulphuric acid mixture is again sprayed on the shot and the cycle repeated. This is continued as long as the copper sulphate liquor leaving the tanks is of the right gravity.

The first liquor coming from the solution tanks is heavy in copper sulphate; this diminishes as the oxide and sulphate salts are gradually consumed from the surface of the shot. After the solution has flowed 3 or 4 hr. over the shot, it is so weak in copper sulphate that it is no longer economical to continue it over the tank. Another solution tank must be started, and the former one put on the oxide period of the cycle.

Liquor leaving the oxidation and solution tanks passes through a wooden launder to the top of the lead-lined wood settling tanks. The first tank will have the heaviest sediment of impurities, while those after the third will have hardly any. All slime, insoluble sulphates or metallics, and dirt which have been carried from the dissolving tank will settle in these tanks; hence the liquor leaving them is freed of impurities which would otherwise be entrained in the copper sulphate crystals if they reached the precipitation tanks.

To ensure continuous operation, the same number of crystallizing tanks must be filled as are pulled for crystal production. Upon removal of the crystals from the tank, they are taken to the centrifugal floor for washing. The crystals are delivered to a trommel, where sizing is effected. Copper sulphate should be barreled immediately after washing and sizing, as it is efflorescent.

Handling

Cypress and red wood are used as storage tanks for acid solutions of copper sulphate. Worthite and Durimet equipment is in plant use for handling copper sulphate plus 10 per cent sulphuric acid at 200°F.

A high-silicon iron pump is used in some plants. Hard rubber can be used. Other pump materials in service include lead, 18-8 Mo and stabilized 18-8 columbium stainless steel. The last gives good service even in the presence of acid because copper sulphate acts as an inhibitor.

Lead is widely used for tank linings in electroplating. Inconel in some cases is excellent.

Packaging

Copper sulphate is packed in unlined wood barrels for shipment.

CRANBERRIES

The processing of cranberries once presented many difficulties because of active reactions from the fruit acids, but stainless steel now helps to assure the retention of the original color and flavor without damage to the equipment.

A stainless-steel hopper is used in a cranberry-canning plant to measure the berries before they are cooked. From the hopper they go to a stainless-steel kettle, where they are cooked. Other stainless-steel equipment is used to handle the berries in preparation for the cans.

CROTONALDEHYDE

Crotonaldehyde has a very pungent, suffocating odor. It is used as a raw material in the production of many organic syntheses, as a solvent in synthetic resins, and as an intermediate in the rubber and dye industries.

Production

Materials of Construction.—At the Wacker's Burghausen plant the crotonaldehyde recovery still was cast iron, the dephlegmator was made of Type 304 stainless steel, the head product condenser was made of the same metal, and the reboiler was Type 316 stainless steel. (Brundrit, D., A. W. C. Taylor, and J. F. Ellis, German Acetylene Chemical Industry Acetaldehyde Manufacture, PB 79186, p. 46, Office of Technical Services, U.S. Department of Commerce.)

Different materials of construction were used at the Bunawerke, Schkopau, Germany. (Wood, Lt. Col. W. L., Production of Acetylene at the Bunawerke, Schkopau, Final Report 75, British Intelligence Objectives Sub-Committee, His Majesty's Stationery Office, London.) In the separation of crotonaldehyde and acetaldehyde the aqueous solution of the two flows to a point one-third the way down from the head of a high column packed with rings. Live steam is admitted at the base, giving pure acetaldehyde as a product, reflux being provided. Leaving the kettle is a 4 per cent solution of crotonaldehyde in water. This solution is passed to the mid-point of a similar column, heated by a closed steam coil. Water flows to waste from the base, while 85 per cent crotonaldehyde is taken off as product. Construction of this part of the equipment is of copper or aluminum throughout.

Process.—Crotonaldehyde is the normal product of the condensation of acetaldehyde when this is accomplished by use of hot sodium acetate solutions. It is also formed if aldol is heated.

Packaging

Crotonaldehyde is shipped in steel drums.

CYANACETAMIDE (C AMIDE)

Aqueous ammonia is charged to an enameled kettle and cooled to −10°C. Cyanacetic methyl ester is run in during about 3 hr. with cooling to 10 to 15°C.

The batch is then stirred overnight while cooling to −12°C., and from time to time the walls of the pan are scraped with a wooden scraper to remove crystalline deposit.

In the morning the batch is blown to a nutsche, filtered, and the pan washed out. The nutsche cake is transferred to a centrifuge to expel liquor as far as possible, fumes being taken away by an exhaust hood. The centrifuged mass is transferred as rapidly as possible to drying trays and dried in a current of air at 40 to 45°C. for 12 hr., then for 6 to 8 hr. at 60°C. (Adams, D. A. W., and W. Baird, Some Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.)

DIBUTYL METHYLENEDITHIOGLYCOLATE

Dibutyl methylenedithioglycolate, known as plasticizer 88, is used with polyvinyl chloride. The following information is based on documents obtained from I.G. Farbenindustrie at Leverkusen and Ludwigshafen. (Slade, G. Herman, Plasticizers for Polyvinyl Chloride, B.I.O.S. Trip 2759, 1946, British Intelligence Objectives Sub-Committee, His Majesty's Stationery Office, London.)

Production

Materials of Construction.—The initial formation of sodium chloracetate must be carried out in suitable acid-resisting equipment which can be either glass-lined or acid-resisting enameled cast-iron equipment. Provision is made for cooling with acid-resisting cooling coils. This glass-lined equipment can be an open vessel, but it must be fitted with a stirring device. Condensation of sodium chloracetate can be done in enameled, leaded, or stainless-steel vessels, which must also have provision for cooling. Liberation of the glycolic acid with sulphuric acid can be done in a similar vessel; for the final esterification, stainless steel is preferred. For this reaction, a closed stainless-steel kettle is necessary, with provision for return of butanol after passing through an automatic decanter in order to remove water of dehydration and the water formed during esterification.

Process.—Chloracetic acid is dissolved in water and neutralized with 50 per cent caustic solution, the temperature being held by cooling coils at 10°C. maximum. When the reaction is complete, the temperature is allowed to rise to 20°C. and the mixture should then be slightly alkaline. This solution is subsequently mixed with sodium thiosulphate solution. The temperature is held at 30°C. and after 2 hr. is allowed to rise to 50°C. It is continuously stirred throughout the process. It is then cooled to 30°C. and mixed with 60°Bé. sulphuric acid, then with 30 per cent formaldehyde solution and finally 60°Bé. acid. It is then heated for 3 hr. to 60°C.

The mixture is subsequently cooled to 15 to 20°C., whereupon a portion crystallizes which is filtered off. These crystals are washed with water.

The methylenedithioglycolic acid is mixed with butanol. To this is added sulphuric acid and sodium sulphate, and this mixture esterified. The material is heated until distillation begins, when butanol and water will pass over. These are condensed and run through an automatic separator, so that the water is run to waste and butanol returned. In order to complete esterification, more butanol can be added, and at the end of 10 hr. the temperature will have risen to 120°C., when esterification is complete. The mixture is then heated to 140°C. in order to distil off unchanged butanol. The sample of the ester should have an acid number of less than 70.

The material is heated to 150 to 160°C. in vacuum until no more butanol passes over. The remaining plasticizer is clarified and filtered by bleaching earth.

DIBUTYL THIODIGLYCOLATE

Dibutyl thiodiglycolate, known as plasticizer 77, is used for polyvinyl chloride. The following information is based on documents obtained from I.G. Farbenindustrie, Leverkusen, Germany. (Slade, G. Herman, Plasticizers for Polyvinyl Chloride, B.I.O.S. Trip 2759, 1946, British Intelligence Objectives Sub-Committee, His Majesty's Stationery Office, London.)

Production

Materials of Construction.—The reaction is in many ways similar to dibutyl methylenedithioglycolate described previously. The neutralization of the chloracetic acid with caustic soda is best carried out in a suitable acid-resisting enamel or glass-lined vessel with efficient cooling coils. The liberation of the free acid by sulphuric acid can be done in a lead-lined vessel or any acid-resisting enamel vessel. The esterification can be carried out in either glass-lined or stainless-steel vessels.

Process.—This material is produced by the reaction of sodium sulphide on sodium chloracetate, which when neutralized with sulphuric acid yields thioglycolic acid. This can be esterified with normal butanol to yield dibutyl thioglycolate.

Chloracetic acid is dissolved in water and cooled to less than 10°C. With cooling and thorough stirring, caustic soda of 30 per cent is added, the temperature not being allowed to rise above 10°C.; the solution after adding caustic soda should be neutral or slightly alkaline. It is reacted with sodium sulphide over a period of 10 hr. In order to keep the temperature down, the vessel must be cooled with water. Finally, it is heated for 2 hr. from 40 to 45° until a sample shows no free sodium sulphide when tested with lead acetate paper. The sodium thiodiglycolate as prepared is run into water, and to this is added sulphuric acid, 60°. The temperature is allowed to rise to 40°C.

The solution of the free thioglycolic acid is mixed with butanol and stirred at 45°C. The butanol layer after separation is run to the esterification vessel. Two further extractions with 800 kg. of butanol are carried out. The first of the two is run also to the esterification vessel, but the second is set aside to be used for the first extraction in the following reaction.

The acid water after three extractions of diglycolic acid is now heated in the esterification vessel and begins to boil at 97°C. The water vapor is run through a condenser and through an automatic decanter, so that the lower water layer is run to waste and the butanol layer is returned. At the end of approximately 20 hr. the boiling temperature will have risen to 116°C., at which temperature the esterification is complete and the excess butanol is removed under vacuum. The crude dibutyl ester is cooled to 20°C. and stirred with sodium carbonate until neutral. After the sodium sulphate has crystallized out, the clear solution is distilled under vacuum, utilizing water at 30 atm. pressure as heating medium. At 170 to 180°C. the dibutyl thiodiglycolate will distil.

DICHLOR-DIPHENYL-TRICHLOROETHANE

This chemical which is commonly called DDT is an insect killer. The pure product is a white waxy powder with a faint, fruitlike odor.

Production

Materials of Construction.—Glass-lined steel equipment is said to be preferable, but some other materials are in use. For example, Moull piping is used for reactor blow legs in condensation units.

Process.—The chlorinator, preferably of glass-lined steel, jacketed one-piece closed design, is charged with absolute alcohol (denatured with 0.5 per cent benzene) and the temperature reduced to approximately 0°C. Chlorine gas is introduced at this point. The temperature is brought up to 50°C. (Information on this chemical supplied by P. A. Laird.)

The unabsorbed or excess chlorine passes to the condenser, preferably glass-lined, with some of the unreacted alcohol where it is largely refluxed back to the chlorinator. Resultant heavy heat evolution is controlled below 30°C. by brine in the jacket. When the rate of heat evolution drops suddenly, the brine must be drained quickly from the jacket and the batch temperature allowed to rise to 45 to 50°C. gradually. Then the batch in the chlorinator is held at 50°C., and the chlorine rate increased with the temperature increasing to 55°C., where it is held for 1 hr. and then allowed to increase to 75°C. within the next hour, where it is maintained until the batch is one-half chlorinated.

After 24 to 26 hr. the specific gravity should be 1.35 to 1.38. Chlorine is then turned off.

The second half of the chlorination is started at 75°C., and the temperature allowed to rise at the rate of 1°C. per hr. to 90°C., where it is held until chlorination is completed. Chlorination is considered complete when the chlorine content of the exit gas from the chlorinator reaches 10 per cent as 60 lb. per hr. of chlorine is being fed to the chlorinator. Specific gravity should not exceed 1.515 at the end point, although specific gravity alone is not an absolute indication of completion.

After the batch is completed in the chlorinator, it is heated to 92°C. for 30 min. to evolve some of the dissolved HCl. Then it is cooled to below 50°C.

and dropped to the still. The chlorination reaction is C_2H_5OH plus $3Cl_2$—CCl_3CHO plus 3HCl.

To the alcoholate in the still, 70 per cent of its volume of 95 per cent sulphuric acid is added, and the resulting chloral distilled into a receiver. A glass-lined steel still, condenser, and receiver are definitely preferred because of the free HCl and Cl_2 present. Distillation is completed when the batch in the still reaches 130°C. The waste acid held in the still is discharged to a neutralizing vat and then to the drain.

The empty still is cooled to 50°C. or lower, the crude chloral returned from the receiver and redistilled into the first receiver until the temperature reaches 95°C. as the "cutting" point. The balance is distilled into a second receiver as refined chloral—this is the portion used for making DDT.

The chloral, so distilled, is mixed with monochlorbenzene in a closed, agitated, jacketed reactor, preferably of glass-lined steel, and then 98 per cent sulphuric acid is added with thorough agitation.

This reaction is an exothermic condensation wherein the batch temperature is controlled at 30°C. maximum, after which the temperature gradually drops to room temperature. More monochlorbenzene is then added. The mass then contains solid particles that are somewhat flocculent and tend to float unless thoroughly agitated.

The cooling can be hastened by the addition of crushed ice or by brine cooling in the jacket space.

A typical condensation procedure would be as follows:

1. Charge 2,420 lb. of chloral to the reaction kettle.
2. Then run in 3,855 lb. of monochlorbenzene with agitation of the chloral.
3. Next add rather gradually 6,560 lb. of 98 per cent sulphuric acid with agitation of the reaction mass.
4. Finally, run in 5,130 lb. of 20 per cent oleum with continuous agitation of the reaction mass.

The temperature must not exceed 30°C., and an average temperature of 20°C. is preferred during condensation. When the reaction is completed, add 3,855 lb. more of monochlorbenzene. This should produce a yield of 90.1 per cent DDT based upon the chloral used. The setting point should be 89.9°C., otherwise known as the "solidifying point," as representative of a good final product.

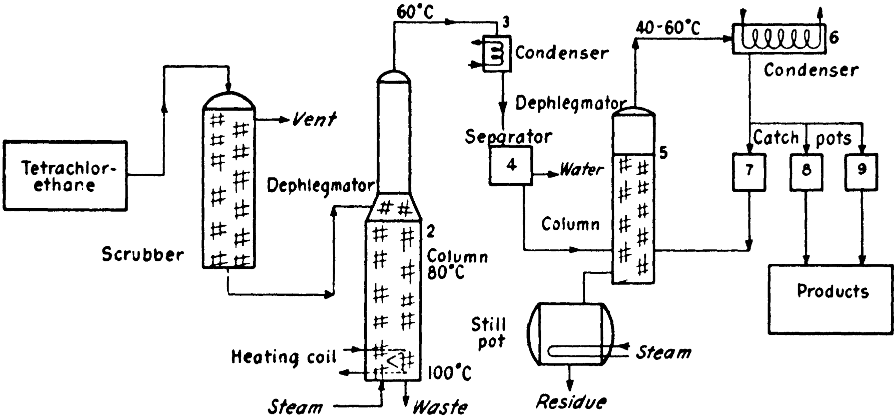
The diluted suspension of DDT is discharged to a centrifuge where the DDT solids are caught and washed with water until acid-free. The DDT solids are then dissolved in and crystallized from ethyl alcohol, forming fine white crystals that are filtered out and dried in a shelf dryer, after which the product is packaged for use or sale. The alcohol is all recovered and purified by distillation for further use. The diluted acid from the hydrolysis is neutralized and discarded. The HCl gas from the chlorination is recovered by absorption.

Packaging

DDT is shipped in paper bags and fiber drums.

DICHLORETHYLENE

Dichlorethylene is produced from tetrachlorethane by reaction with iron turnings. (Carpenter, G. B., Chlorinated Hydrocarbons from Acetylene, FIAT Final Report 843, Technical Industrial Intelligence Division, U.S. Department of Commerce.)



Dichlorethylene.

1. Cast iron
2. Cast iron with copper heating coil
3. Cast iron
4. Cast iron
5. Cast iron
6. Cast iron
7. Cast iron
8. Cast iron
9. Cast iron

Production

Materials of Construction.—Ordinary cast iron and steel are satisfactory for fabrication of equipment except that a copper auxiliary coil is used in the reaction column.

Process.—Tetrachlorethane at a rate of 70 kg. per hr. is first used to scrub the vent gas from the process and then charged to the top of a cast-iron column filled with iron turnings. Live steam is introduced at the bottom, and an auxiliary copper heating coil also supplies heat at the bottom. A water solution containing 2 to 5 per cent ferrous chloride is sent to the sewer from the bottom of the column. The bottom temperature is 100°C., and the temperature of the iron turnings 80°C.

Above the feed point is a section of the tower packed with raschig rings, and on top of this is a dephlegmator. The constant-boiling mixture of dichlorethylene and water leaves the dephlegmator at 60°C., is condensed in an iron condenser, and the water layer sent to the sewer.

Conversion is substantially complete, and the consumption of iron turnings amounts to a kilogram per kilogram of dichlorethylene produced.

The crude dichlorethylene from the separator is charged to a packed iron column, together with the heads fraction from the trichlorethylene plant. The column is heated by a steam coil in the still pot and equipped with a dephlegmator. It is operated partly continuous and partly batch. The still residue is sent to the batch still of the trichlorethylene plant.

Two fractions are separated: one pure *trans*-dichlorethylene and the other pure *cis*-dichlorethylene.

DICHROMATE—SULPHURIC ACID

Glass tanks are in use for a pickling solution containing 10 per cent sulphuric acid and 8 per cent dichromate at 120°F.

DIHYDROXYDIPHENYL SULPHONE

It has been reported that the German I.G. Farbenindustrie was making dihydroxydiphenyl sulphone at its Ludwigshafen plant. (Adams, D. A. W., and W. Baird, Some Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.) This product is 4:4-dihydroxydiphenyl sulphone with small amounts of the 2:4 isomer as impurity.

Production

Materials of Construction.—The following materials and equipment were in use:

1. Cast-iron stirred, pressure vessel fitted with steam as well as cooling water
2. Stirred, tile-lined vessel with lead cooling coil and steam inlet
3. Condenser for distillate from (2)
4. Small separator for separating chlorbenzene-dichlorbenzene from water
5. Measure vessel for chlorbenzene-dichlorbenzene mixture
6. Condenser for steam distillate
7. Horizontal, iron pressure vessel for chlorbenzene-dichlorbenzene mixture
8. Two tiled nutsches
9. Homogeneously lead-lined pressure vessel for mother liquors

Process.—Pure molten phenol is charged to the pressure vessel (1). The temperature is adjusted to 45°C., and oleum run in. Pure *o*-dichlorbenzene-dichlorbenzene mixture from a previous batch is added. The mixture is heated to 150°C., at which temperature a mixture of chlorbenzene-dichlorbenzene and water begins to distil. The vapors are condensed in (3), the water and solvent separated in (4), and the solvent returned continuously to the reaction pan via a siphon. The water is run to a cask for weighing. The temperature is gradually raised to 160 to 162°C. When the distillation of water ceases at this temperature, chlorbenzene is added, and this addition is repeated twice to complete the removal of water. When this point is reached, the contents of the kettle are diluted with *o*-dichlorbenzene (or recovered mixture) and run to kettle (2) previously charged with water. The charge is made faintly alkaline by addition of soda ash and solvent removed by steam distillation. The vapors are condensed in (6), and solvent separated from water continuously in (7). The solvent runs to the pressure receiver (8) from which it is blown without further treatment to measure vessel (5) for the next batch. The kettle contents are then cooled to obtain the sulphone in a good crystalline form, and the product filtered on the nutsches (9). After being washed with water, the sulphone is put into casks.

DI-(*p*-CHLOROPHENYL) METHYL CARBINOL

A recently developed miticide has as its active ingredient di-(*p*-chlorophenyl) methyl carbinol (DMC). The reactions involved in the preparation of di-(*p*-chlorophenyl) methyl carbinol include a Friedel-Crafts synthesis of an intermediate compound, *p,p'*-dichlorobenzophenone, and a Grignard reaction to form the final product. (Savage, R. L., R. Q. Wilson, and J. E. Yocom, Process Development of DMC, New Miticide, *Chem. Ind.*, Vol. 64, No. 3, pp. 392–393, 1949.)

Production

Materials of Construction.—To enable the equipment to withstand the numerous adverse effects of hydrochloric and sulphuric acids, hydrogen chloride gas, and hot toluene and carbon tetrachloride vapors, it was necessary to employ special materials of construction. The neoprene gaskets used between the flanges of the glass-lined equipment had to be replaced with Teflon gaskets. It was also necessary to face the neoprene diaphragms in the diaphragm-type valves with Teflon sheeting.

Glass-lined steel and stainless steel were used for reactors. One glass-lined reactor in the pilot plant had such glass-lined auxiliary equipment as a receiver, a charging tank, a packed tower with by-pass, and a condenser. All pipe lines connected with this unit were glass-lined.

Not only was stainless steel used for a reactor, but it was also used for filter presses and charging tanks. Some piping was Saran.

Process.—The Friedel-Crafts reaction was carried out by adding a mixture of chlorobenzene and carbon tetrachloride to a glass-lined reactor containing carbon tetrachloride and anhydrous aluminum chloride. The reaction is exothermic. After addition was complete, the reaction mixture was stirred for 3 hr. in a temperature range of 25 to 30°C. Hydrogen chloride gas liberated was absorbed in a packed tile tower. The acid formed was neutralized by passing it through neutralizing towers filled with limestone. The conveying pipes were Saran.

Excess carbon tetrachloride and unreacted chlorobenzene were removed by steam distillation, leaving a viscous oily residue containing di-(*p*-chlorophenyl) dichloromethane and its isomers. These substituted methanes were hydrolyzed to the ketone by refluxing the isopropyl alcohol. The hot slurry was pumped to a stainless-steel reactor, where it was cooled with brine to 0 to 5°C. and the *p,p'*-dichlorobenzophenone crystals and the *o,o*, and *o,p* isomers not dissolved in the alcohol formed a semisolid mass on the bottom of the reactor. The isopropyl alcohol containing some of the *o,o* and *o,p* isomers was pumped off, and the residue in the reactor was reslurried with naphtha. The naphtha slurry was filtered in a stainless-steel horizontal-plate filter, then washed with fresh naphtha and with aqueous isopropyl alcohol, which removed the remaining isomers. The solid *p,p'*-dichlorobenzophenone obtained represented 35 to 40 per cent of the theoretical yield.

The intermediate compound was removed from the filter press, weighed, and charged to the glass-lined reactor together with toluene, water, and soda ash. The mixture was heated to boiling with agitation. The *p,p*-dichlorobenzophenone dissolved in the toluene, and the aqueous sodium carbonate solution neutralized any acid present. The lower aqueous layer was pumped off, and the toluene solution dried. It was pumped to a stainless-steel charging tank, and methyl magnesium bromide in butyl ether was pumped into the dry reactor. The toluene solution was added to the Grignard reagent over a period of 70 to 90 min. After the addition period, the mixture was refluxed for 1 hr. to complete the reaction.

The reaction mixture was cooled to 40°C., and the Grignard complex hydrolyzed by adding an aqueous ammonium chloride solution. After agitation the aqueous layer was pumped off and the oily layer containing the di-(*p*-chlorophenyl) methyl carbinol and solvents was given a 2 per cent aqueous sodium carbonate wash.

The toluene and butyl ether were removed by steam distillation. The molten product remained in the kettle and was drained from the reactor and allowed to solidify. The yield of di-(*p*-chlorophenyl) methyl carbinol ranged from 85 to 90 per cent of the theoretical.

DIMETHYL SULPHATE

Dimethyl sulphate is not corrosive if it is anhydrous, but if moisture is present, hydrolysis results and sulphuric acid forms. Therefore, it must be stored in closed containers or blanketed with an atmosphere of dry air or nitrogen at all times.

Packaging

This chemical can be shipped in glass bottles closed with ground-glass stoppers and cushioned with incombustible absorbent material within a hermetically sealed metal can, the can to be similarly cushioned within a wooden box. Other containers are metal drums and tank cars.

DIPHENYL

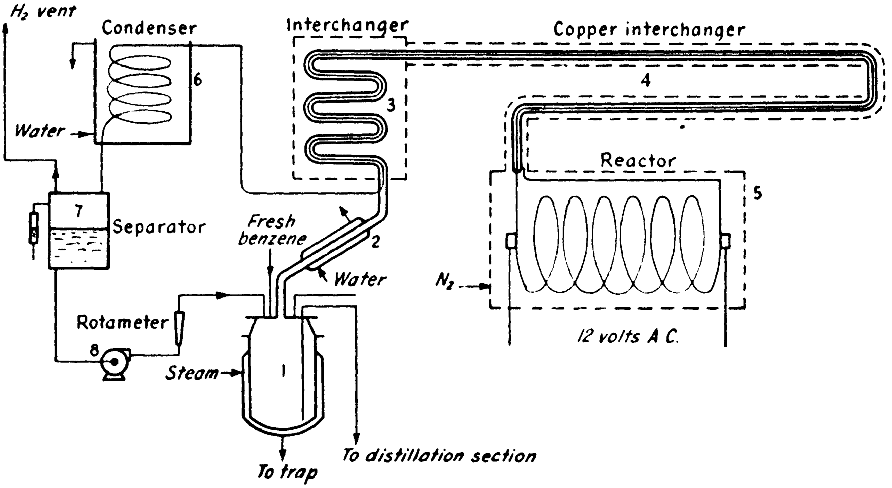
Diphenyl was found after the war to have been made at Leverkusen, Germany. (Clough, G., Manufacture of Diphenyl at I.G. Farbenindustrie, A.G., Leverkusen, Final Report 1787, British Intelligence Objectives Sub-Committee, His Majesty's Stationery Office, London.)

Production

Materials of Construction.—The first interchanger is mild steel and is welded to the second interchanger, which is copper. A steel coil was found to give heavy deposits of carbon, but copper tubing gives only very slight deposits. To increase the mechanical strength of the equipment an alloy containing 2 per cent manganese is used rather than pure copper. The manganese had no bad effects on the reaction.

The copper interchanger is welded to the reactor coil of copper manganese tubing. The helical coil is mounted on a horizontal firebrick core.

Process.—Benzene vapor is heated to 800°C. for 2 to 3 sec. at essentially atmospheric pressure in a copper tube and is thereby decomposed to diphenyl and ter- and poly-phenyls. Conversion per pass is some 10 to 15 per cent. The condensable products are separated from the hydrogen which is produced and returned to the benzene evaporator in order to recycle unconverted benzene. The liquid in the evaporator becomes richer in diphenyl, and periodically batches are removed and distilled to give benzene, pure diphenyl, and diphenyl residues.



Diphenyl.

1. Iron
2. Steel
3. Mild steel
4. Copper, 2 Mn
5. Copper, 2 Mn
6. Mild steel
7. Steel
8. Steel

In somewhat more detail the process is as follows: In order to minimize corrosion of the copper equipment it is important to use a benzene of low-sulphur content. Purchased benzene is therefore washed with 96 per cent sulphuric acid to remove carbon bisulphide and thiophene. The pure benzene goes to an iron evaporator. The vapor from the evaporator is led through a short inclined length of water-jacketed line; this causes return to the evaporator of a small amount of condensate, which contains the greater proportion of the high-boiling materials vaporized along with the benzene. Benzene vapors then pass through the outer tube of a concentric iron tube heat interchanger. Flow is countercurrent to the hot reaction products passing through the inner tube. In the first interchanger, the benzene vapors are heated from 6 to 530 to 535°C., the products being cooled to 145 to 160°C. The benzene vapors are further heated to 650°C. in a copper-manganese heat interchanger.

In the reactor itself, the temperature rises from 650 to 790 to 800°C. The reaction products are passed through the inner tubes of first the copper and then the iron heat interchangers. They are then condensed in a mild-steel water-cooled coil and run to a small separator from which hydrogen is vented to the atmosphere. Diphenyl solution passes through a wire gauze filter to remove carbon particles and is returned to the evaporator by a centrifugal pump.

As required, liquid is egged from the evaporator to the benzol recovery still, where, on heating to 130°C., most of the unconverted benzene distils over and leaves behind the crude diphenyl. Pure diphenyl is fractionated from the crude in a still.

DIPHENYLPROPANE

British and American engineers investigating German chemical manufacturing processes after the recent war have reported on the production of this chemical in two plants. The principal difference in the two methods was the catalyst. In one case sulphuric acid was used, and in the other hydrochloric acid. But this difference had an effect on the materials of construction as would be expected.

Production

Materials of Construction.—In the I.G. Farben.'s plant at Ludwigshafen diphenylpropane was made by condensing phenol with acetone, using hydrochloric acid as catalyst. (Adams, D. A. W., and W. Baird, PB 80401, Office of Technical Services, U.S. Department of Commerce.) The reaction kettle was a rather shallow glass-lined pan. It carried an anchor stirrer. The hydrochloric acid gas came via an iron pipe line and was fed by means of a rubber-covered iron pipe to the bottom of the pan.

The Chemische Werke Albert at Wiesbaden-Biebrick, Germany, was reported as having used the sulphuric acid catalyst. (Slade, G. H., Synthetic Resins for Surface Coatings, B.I.O.S. Report 1794, Item 22, British Intelligence Objectives Sub-Committee.) A lead-lined closed kettle fitted with lead-lined cooling coils was used.

Process.—In the plant at Wiesbaden-Biebrick dilute sulphuric acid is run in and the phenol is added at 30°C. This addition takes place over 1 hr. The temperature is then reduced to 25°C., and within the range of 25 to 30° the acetone is added with cooling and stirring. When all has been added, the temperature is allowed to rise to 40°C. It is then held at 40°C. for 40 hr., when the diphenylpropane crystallizes. It is filtered and finally washed at least three times with water and finally with dilute ammonia. It is subsequently dried and should have a melting point of 154 to 156°.

In the Ludwigshafen plant the reaction mixture becomes exceedingly viscous toward the end of the reaction, and the stirring is then carried out intermittently. When stirring is no longer possible, the reaction is ended. Water is then run into the pan, the mass broken up by stirring, and the product run to the nutsche.

DRY COLORS

A modern dry-color plant is typified by the Brooklyn plant of Reichhold Chemicals, Inc. Pigments produced in this plant include the chrome yellows and oranges, iron blues, zinc chromate and chrome greens. (Callaham, J. R., Modernizing Chemical Color Manufacturing, *Chem. & Met. Eng.*, Vol. 50, No. 6, pp. 106–111, 1943.)

Production

Materials of Construction.—Much wooden equipment is in use. It includes such pieces as dissolving solution tanks, precipitation tanks, and filter presses. Lead-lined tanks are used for dissolving treating agents. Drying trays are made of aluminum or enameled steel.

Process.—Basic equipment used in the manufacture of all the principal dry colors is fundamentally the same, although slight modifications in the processing procedure results in some changes in layout.

The open dissolving or "striking" solution tanks are of wooden construction with two wooden cross blades and baffles on the sides for more effective agitation. These stirring devices are now direct gear drives. Here the basic raw materials are dissolved at a definite and controlled rate by centrifugal pumps into another similar wooden tank of larger size, where precipitation of the basic pigment occurs.

Treating agents, which may be acids or alkalis, oxidizing agents, or other chemicals, are dissolved in small open tanks, usually lead-lined and provided with a small high-speed, side impeller agitator. Small centrifugals pump the treating solutions into the precipitator at a predetermined rate and during agitations. Durimet 20 pumps have been successfully applied for this service.

A major improvement in processing is that of accurate pH and temperature control throughout the precipitating and digesting steps. All production in each department is regulated from a single control panel equipped with multipoint pH- and temperature-control instruments. Flow rates of all solutions are controlled by flowmeters and adjusted by valves located in the central panel. Drying temperatures are carefully controlled by automatic instruments equipped with dial and pointer adjustment.

After color precipitation, digestion, and washing by decantation, the slurry is pumped into batteries of wooden plate-and-frame filter presses. Heavy cotton canvas is used as the filtering medium. Cakes of about 1.5 in. are built up and then washed free of soluble salts by water.

Throughout the steps of precipitation as well as digestion and washing, processing conditions for the basic colors and for some of the different shades all differ, for it is in these phases that the fundamental characteristics of the pigment are developed. However, handling operations, which involve filtering, drying, pulverizing, blending, and packaging, are fundamentally the same for all products, so that the following paragraphs may be applied equally well to iron blues, chrome yellows and oranges, chrome greens, zinc chromate, and organics.

Filter presses are opened by hand, the cakes of wet pigment placed in shallow aluminum or enameled steel trays and loaded on small frame trucks equipped with wheels. Each truck holds 40 trays with air space of about 3 in. between trays. These are pushed by hand to a battery of centrifugal fan-type dryers, each of which holds six such trucks. Here air heated to 185 to 212°F. by steam coils is circulated until the moisture content of the cakes is reduced to the neighborhood of 1 to 2 per cent, a process usually requiring some 20 to 30 hr.

The trucks of dried colors are returned to an upper floor, where the trays are dumped into precrushers provided with exhaust hoods, where lumps are broken up. The material is then fed into high-speed hammer mills of the micropulverizer type. These are run by squirrel-cage motors and charge large conical blenders located on the floor below. There are three such mill rooms, one for organic reds; another for the greens, blues, and purples; while the third is used for chrome yellows and oranges.

All material is ground to pass 100 per cent through a 325-mesh screen. Some materials which do now require blending are precrushed into the hoppers on the ground floor and pass directly into barrels or other containers.

If, after grinding, a batch is slightly off shade or if other materials are to be blended in, the pigment is charged into one of the two double-cone mixers rotated on trunnions and provided with a magnetic brake mechanism. For special blends, a double-helical ribbon mixer is provided.

Packaging

Zinc chromate is for the most part packaged in multiwall paper bags from the bag-packing department.

EGG POWDER

An improved process and equipment have been developed by a joint effort of many organizations. (Greene, J. W., R. M. Conrad, A. L. Olsen, and C. E. Wagoner, Production of Stable Spray-dried Egg Powder, *Chem. Eng. Progress*, Vol. 44, No. 8, pp. 591–601, 1948.)

Production

Materials of Construction.—The galvanized sheet-iron spray dryer is of a design similar to the Douthitt (now Swenson) dryer. The lid is also galvanized iron. All interior seams are solder-wiped, and several coats of a phenolic enamel are applied and baked on the inner surfaces.

A cyclone-type redryer is constructed from sheets of cellulose acetate. A receiving jar is below the truncated cone and provides a means of collecting the powder.

A premixed air-natural-gas mixture is fired in an aluminum oxide refractory tube with a steel jacket situated in a brick-walled furnace. Hot combustion gases and diluent air are drawn from the furnace and forced into the cyclone by means of a blower. A high-pressure pump is used for the homogenization of liquid whole egg prior to drying. All liquid-line connections and feed lines are stainless steel. Tips on the spray nozzle are made of high-carbon steel and carefully hardened.

Monel breaker arms and pans are used in some plants making egg powder in mechanical egg-breaking machines. And Monel chutes and hoppers are in use to collect egg powder from the dehydrating chambers.

Process.—Eggs are broken, stirred, and filtered through a porous cloth. The mixture is cooled from 50 to 60°F. to 35° promptly. The liquid is passed through an homogenizer and sent to the dryer, where it is sprayed. The exhaust temperature is 140 or 180°F.

The dried material settles as a fine powder on the sides of the cyclone. It passes through the redryer. In order to restore the normal pH of the acidified powder during reconstruction, sodium bicarbonate can be added to the dry powder.

ESSENTIAL OILS

There are several metals that can be safely used where any contact with essential oils is permitted. These metals are aluminum, nickel, Monel, Inconel, stainless steel, silver, and tin. All others ruin the flavor of essential oils in a surprisingly short time. In some cases the flavor loss is complete in overnight contact. Iron and copper are particularly active in bringing about such flavor losses.

In many cosmetic plants aluminum bottles are used for handling essential oils. The advantage of aluminum bottles is that the metal has no effect on the oils and is superior in mechanical strength to that of glass bottles.

A manufacturer of essential oils writes, "We are using nickel equipment to produce the following products: benzyl alcohol, benzyl acetate, benzyl salicylate, cetyl alcohol, laurine, thymol amyl cinnamic aldehyde, linalyl acetate, tespinyl acetate, citral, cinnamic aldehyde, heliotropine cinnamic alcohol, ionones, and methyl ionones."

Yet another manufacturer of essential oils contributes the following, "We are still enthused about the use of Monel in the handling of our various products. It is not injurious to most essential oils and aromatic chemicals. There are a few exceptions, however, among them being: balsam copaiba U.S.P., oil cajeput U.S.P., MM & R, oil cassia redistilled U.S.P., oil cinnamon Ceylon MM & R. For these products we find that chromium-bearing alloys such as stainless steel or Inconel are preferred for storage and handling purposes."

Glass-lined steel is often used for storage of essential oils.

Packaging

Aluminum containers are used for export shipment of high-priced perfume oils and terpeneless oils. Oil of peppermint and oil of wintergreen are shipped in aluminum drums.

ETHANOLAMINES

The plant used by the Germans for making ethanolamines comprises essentially an iron reaction tower carrying an internal cooling coil in the lower part and attached to an external cooler through which the liquid in the reaction tower is circulated. (Adams, D. A. W., and W. Baird, Some Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.)

Production

Process.—For monoethanolamine, 30 per cent aqueous ammonia is charged to a tower and the circulating pump started. Ethylene oxide is then fed into the bottom of the tower. When the addition is complete, the reaction mixture is kept circulating at 35 to 40°C. for a further hour. Ammonia and then water are distilled off; the aqueous monoethanolamine for runnings is collected up to 60°C. per 15 mm. The residue, consisting of about 60 per cent diethanolamine, 30 per cent triethanolamine, and 10 per cent aminoethers, is mainly sold as the base of emulsifying agents. Some, however, is distilled to give diethanolamine (150 to 160°C. per 8 to 10 mm.), and the residue goes to make emulsifying agents, *e.g.*, for floor polishes where color is of little importance.

For making triethanolamine, 30 per cent aqueous ammonia is charged to the tower and reacted with 1,750 kg. of ethylene oxide. After circulating, the product is distilled to remove ammonia and water, the residue being technical triethanolamine. It contains about 5 to 10 per cent diethanolamine and 10 per cent aminoethers.

The color of this product depends on the purity of the ethylene oxide used, and this should contain less than 0.05 per cent acetaldehyde. It is also essential to carry out the distillation in glass-lined equipment in the complete absence of iron.

ETHYL ACETATE

This chemical may be made by either batch or continuous process. Several methods will be discussed here.

Production

Materials of Construction.—Copper apparatus is generally used for large-scale esterification, as this metal is fairly resistant both to organic acids and to sulphuric acid when temperature and concentration are not excessive and free oxygen or compounds readily yielding oxygen are excluded. (Groggins, P. H., "Unit Processes in Organic Synthesis," 3d ed., pp. 648–653, McGraw-Hill Book Company, Inc., New York, 1947.) Steam coils, also of copper, are the usual means of heating. In the copper work, autogenous welding is to be preferred to brazing, although silver solder gives fair results. Gunmetal and phosphor bronze are to be preferred to brass, while 18-8 stainless steel can be used on condensers but not in parts where sulphuric acid is used. Monel heater tubes are used in heater sections of esterifying columns.

In Germany, cast-iron reactors, stills, and condensers are used. (Bidlack, V. C., F. J. Curtis, and J. M. Harris, Dr. Alexander Wacker Gesellschaft für elektrochemische Industrie, Burghausen, Germany, OPB Report 208, U.S. Department of Commerce.

Batch Process.—Acetic acid and alcohol are employed in molecular proportions. (Groggins, *loc. cit.*) The catalyst, H_2SO_4, can be added to the still charge or previously blended with the acetic acid. The charge is brought up to boil, and the whole distillate is refluxed for a time by closing the take-off valve. After an hour, the temperature at the top of the column should be 70° for ethyl acetate and remain steady, while the mid-column temperature will gradually show a drop. When the latter indicates that several plates are charged with liquor boiling about 70°C., the take-off valve can be opened to bleed off the ethyl acetate as fast as it is formed and so hold the temperature in the mid-column constant. As the still charge diminishes owing to the formation and removal of ester, more acid and alcohol can be added through the feed weir boxes to keep the still contents nearly constant in volume. This distillate is stored to be purified in a separate apparatus later.

Continuous Process.—In this process the raw materials are first blended in the correct proportions and fed from the feed tank through a preheater into the esterifying column. (*Ibid.*) From the top of this is taken off a mixture of 20 per cent ester, 10 per cent water, and 70 per cent alcohol, while a suitable amount of the same distillate is refluxed back to the column. The ternary mixture taken off passes to the separating column. Here it is rectified by closed steam in the calandria. Part of the condensate is returned as reflux to the top of the column, and the take-off goes to a proportioning mixing device, where it is blended with water, which causes a separation into two layers. These are settled out in the separator tank, the watery portion overflowing back to the lower part of the separating column, whence, blended with the alcohol and water accumulating in the base of this, it is passed by pipe to a point in the esterifying column.

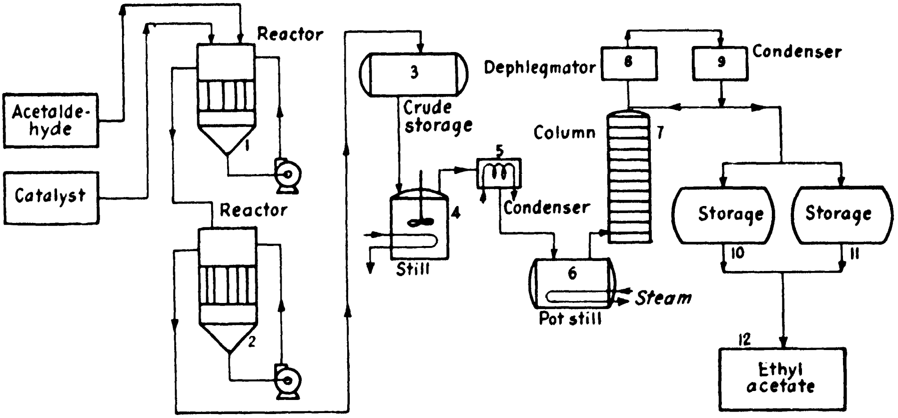
On the lower plates of the column, alcohol is exhausted and distils upward as vapor, while the slop water goes to waste. The washed ester, containing a little dissolved water and alcohol, overflows from the separator and enters the drying column in which a sufficient amount is distilled off to carry with it the water and alcohol, which may go either to the separating column or back to the mixer, washers, and separator. The dry ethyl acetate that accumulates in the calandria of the drying column is taken off through a cooler to the receiving tank.

Wacker Process.—A liquid catalyst, Alal, is used. It is prepared as follows: A steel vessel with reflux condenser on the vent is filled with nitrogen. Zinc-free Alal from a previous run, aluminum chips, and ethyl acetate are added to the vessel. Contents are boiled at 60°C. Chlorine is added to the batch. The boiling is finished when the density of the catalyst is 0.95 to 0.96 at 20°C. After the mixture is pumped into storage tanks, ZnO is introduced and the batch is agitated and ready for use.

Ethyl acetate is made in cast-iron vessels containing cooling tubes. Agitation is effected by pumping around an external circuit. The reaction mixture flows down through the tubes, which are surrounded with brine at −10°C.

The operation is started by putting ethyl acetate and catalyst in the upper vessel. Circulation and cooling are started, and acetaldehyde is added over a period of 1½ hr.

The reaction is followed by the density, which must be kept at 0.95 at 20°C. and must not be allowed to fall lower. The temperature is held at −1°C. When the aldehyde has been added, the contents of the first iron vessel are allowed to overflow into the second and the operation becomes continuous. The crude product is about 98 per cent ethyl acetate. It is distilled from an agitated iron still from which a residue of $Al(OH)_3$ is obtained and discarded. The overflow from the agitated iron still is fractionated batchwise in a copper still and copper column with copper condenser.



Ethyl acetate.

1. Cast iron
2. Cast iron
3. Cast iron
4. Iron
5. Iron
6. Copper
7. Copper
8. Copper
9. Copper
10. Steel
11. Steel

Handling

Aluminum.—Ethyl acetate often is quite acid and contains dissolved heavy metal compounds. For this reason concentrated ethyl acetate often has some action on aluminum, although usually this is not severe enough to preclude the successful use of aluminum equipment for handling this chemical. (Aluminum Co. of America, "Aluminum in Chemical Industry," p. 41, 1944.)

Cast Iron.—A pump of all cast iron is used for handling acetate.

Alloys.—Types 316 and 374 stainless or high alloys such as Worthite or Durimet 20 can be used successfully. Glass-lined steel equipment is unaffected.

Packaging

Ethyl acetate is shipped in steel drums and tank cars. Aluminum tank cars of Alclad 175-T are also used for transporting the acetate.

ETHYL ALCOHOL

Industrial alcohol when pure shows no corrosive action up to its boiling temperature, but under certain conditions in the presence of air and in aqueous solutions it can and does give trouble. Therefore, special materials of construction are used in the production and handling of ethyl alcohol.

Production

Materials of Construction.—Copper is the mainstay of the alcohol industry. It is used primarily because of its corrosion resistance, high-heat conductivity, and ease of fabrication. Copper is used for brew kettles, fermenters, equipment for yeast culture, stills, condensers, columns, cooling coils, storage tanks, and piping. All pumps handling acid-containing materials are bronze. Valves are most generally made of bronze.

Ordinary iron and steel are used to some extent. Fermenters are sometimes made of these metals. Pipe lines handling water are steel.

Wood is favored by some engineers for fermenters and storage tanks. The woods used include cypress, oak, Douglas fir, and red fir.

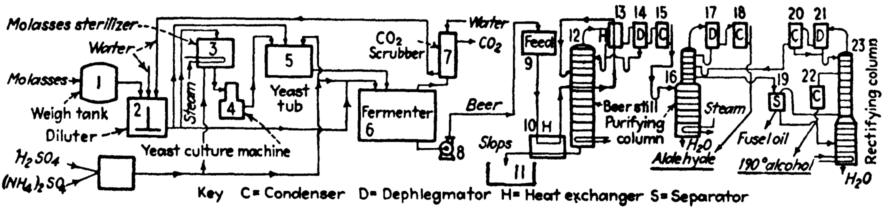
In the manufacture of ethyl alcohol, rectifying stills, columns, heat exchangers, condensers, and piping have been made of Type 304 stainless steel. Type 430 is often suitable for some of the equipment.

Karbate bubble-cap trays, up to 5½ ft. diameter, complete with Karbate caps, chimneys, and downcomers, have been in use for several years in the stripping and scrubbing phases of the concentrated sulphuric acid process for the production of ethyl alcohol from ethylene. (Revilock, J. F., Carbon and Graphite, *Chem. Eng.*, Vol. 55, No. 10, p. 236, 1948.) In the stripping column, the Karbate trays are in contact with ethyl alcohol, ether (both in the liquid and vapor phases), and approximately 50 per cent sulphuric acid at temperatures varying from 150 to 230°F. The Karbate trays in the scrubbing tower are in contact with dilute caustic (1 to 10 per cent) and crude alcohol vapor at a temperature of 212°F. Also in the caustic scrubber, the lining is fabricated from graphite slabs. Other Karbate bubble-cap trays are operating satisfactorily, in the stripping tower of a process similar to that mentioned above for the production of tertiary butyl alcohol.

In the stripping phase of the ethylene to ethyl alcohol process, Karbate tube bundle exchangers are being used in calandria-type boilers for the evaporation of the alcohol and ether from the water solution of sulphuric acid. The shell side is rated for 50-psi. steam.

Ethyl alcohol can and is being produced from several raw materials such as molasses, grain, sulphite-pulp-mill liquors, natural gas, and petroleum.

Molasses Process.—The process steps are as follows: (1) pasteurization of molasses, addition of sulphuric acid, and removal of the precipitated calcium sulphate in solid basket centrifugals; (2) flash cooling the clear mash and diluting with cold water; (3) preparation of the pure yeast culture, propagation in yeast tubs, addition to the diluted molasses, and fermentation; (4) separation of the yeast from the beer in separators, and washing the yeast slurry, and drying; (5) simultaneously dealcoholizing the yeast-free beer and concentrating the stillage in multiple-effect evaporators; (6) recovery of low wines (50° proof) as condensate in the evaporator's second effect and its distillation.



Ethyl alcohol.

1. Iron
2. Iron
3. Copper bearing steel
4. Copper, stainless steel
5. Copper, stainless steel
6. Copper bearing steel, copper
7. Steel
8. Bronze
9. Steel
10. Copper or cast iron
11. Steel or wood
12. Copper, wood
13. Copper, Type 304 stainless steel
14. Copper
15. Copper, Type 304 stainless steel
16. Copper
17. Copper
18. Copper, Type 304 stainless steel
19. Copper
20. Copper, Type 304 stainless steel
21. Copper
22. Copper, Type 304 stainless steel
23. Copper, Type 304 stainless steel

Pumps: bronze for acidified solutions
Piping: copper for beer, slop, etc.; steel for water, molasses, and sulphuric acid
Valves: bronze

Sulphite-waste-liquor Process.—The process used by the Ontario Paper Co., Ltd., at Thorold, Ont., has been described. (Callaham, J. R., From Waste Liquors to War Alcohol, *Chem. & Met. Eng.*, Vol. 50, No. 12, pp. 104–107, 1943.) Waste liquor is pumped from the blow pits near the digesters to a wooden storage tank. This goes through a heat exchanger, where it is cooled to 85°F. Cooled liquor from the wooden head tank is then dropped to wooden neutralizing tanks provided with cone bottoms. The pH is increased to 6.5 by addition of a slurry of slaked lime.

Fermentation is carried out at about 85°F. in units of wooden fermenters. A portion from the bottom of each fermenter is pumped to a wooden head tank from which it flows to a solid bowl centrifugal separator for removal of sludge, which is sent to the sewer. Clarified beer is run to the beer wells.

After fermentation is complete, the liquor is allowed to stand for a few hours for settling of solids, after which it is pumped to a steel tank which feeds the centrifugal separators. The separated yeast is sent to steel storage tanks and then, after treatment, to a new batch of fermenters.

Beer from the yeast separators, together with that from the sludge centrifuge, is sent to wooden beer wells from which the feed for the distillation unit is pumped. At this stage the alcohol content is about 0.7 to 1.5 per cent.

Sulphite-liquor fermented beer is pumped to a beer still, the top of which receives alcohol-water vapor containing about 10 per cent alcohol. This vapor goes to the bottom of the rectifying column. The concentrated and partially refined ethanol, taken from near the top of the rectifying column, is fed to the methanol column for purification. The methanol fraction is removed from the top of this column, and high-purity, 192-proof ethyl alcohol is withdrawn from the base of the column to go to product storage.

Ethylene Process.—The Standard Alcohol Co. and the Standard Oil Development Co., subsidiaries of the Standard Oil Co. (New Jersey), erected a plant to produce ethyl alcohol from ethylene adjacent to the Baton Rouge refinery of the oil company. (Anon., Ethyl Alcohol Made from Refinery Ethylene, *Chem. & Met. Eng.*, Vol. 52, No. 11, pp. 96–98, 1945.)

Ethylene is scrubbed and purified and piped in gaseous form direct to processing in the alcohol plant. On entering an absorber, ethylene comes into contact with sulphuric acid. The resulting liquid is a mixture of monoethyl and diethyl sulphate. Esters leave the bottom of the absorber and are pumped to a hydrolyzer column along with water. Here the esters formed in the absorber are converted to alcohol, ethyl ether, weak acid, and other materials.

Crude alcohol and other products pass to a stripping column. Steam carries off the alcohol, ether, and a small volume of acidic material. This material goes to a caustic scrubber. Vapors of alcohol and ether pass off the top. They are condensed and pumped to the crude-alcohol storage tank.

Ether is removed in the ether column. The overhead, a mixture of ether and alcohol, is water scrubbed. The alcohol is returned to the alcohol column, and the ether is condensed and conveyed to storage. Crude alcohol bottoms are fed into an alcohol column to remove the water. The 192-proof alcohol is removed, cooled, and pumped to storage.

Handling

The peculiar corrosion characteristics of industrial alcohol have been discussed. (Moore, W. C., Industrial Alcohol versus Construction Materials, *Chem. Eng.*, Vol. 55, No. 9, p. 247, 1948.) At temperatures up to its boiling point (78.4°C.) pure ethyl alcohol is probably less corrosive toward iron, steel, and copper than any other common liquid. It also has little or no action on solder, tin, and lead. However, in the presence of air and in aqueous solutions, if couple effects can be set up between two or more of the above metals, corrosion may occur at elevated temperatures, especially with iron, solder, and lead.

Owing to the ease with which the ethylates of aluminum and magnesium are formed, especially at elevated temperatures, ethyl alcohol may be regarded as a corrosive agent for these two metals. This action is enormously increased in the presence of mercury or its alcohol-soluble salts.

Exceedingly small amounts of some impurities may enhance enormously the corrosive action of alcohol, especially toward iron and steel. A certain sample of high-grade alcohol was found to have very little, if any, corrosive action toward sheet steel immersed completely for 51 days. On the other hand, this same alcohol contaminated with only 0.001 per cent (1 part per 100,000) sodium chloride began to corrode a similar piece of steel within 20 min. These tests were made at room temperature. Still another sample of alcohol had practically no action on a piece of steel partly covered by it for a period of 4 years.

Alcohol, originally noncorrosive, may become highly active toward metals if it becomes contaminated during a manufacturing or recovery process. This point was clearly brought out when a considerable quantity of an alcoholic solution of hydrogen chloride was distilled. In the final rectification, samples of the alcohol were taken at intervals and none of these samples responded to the silver nitrate test for chlorides. These samples were combined and used as an antifreeze in two automobiles. The owners of both machines very soon had to purchase new radiators for their cars. Chlorides have also been found to corrode silver very rapidly in alcoholic solutions.

Because of its high solvent action on organic materials, care has to be taken in bringing alcohol into contact with organic substances, not necessarily because it will corrode or dissolve them to a dangerous extent, but mainly to avoid contamination of the alcohol by its acquiring objectionable odors or color. Certain denatured alcohols, however, can be shipped in wooden barrels, which are generally "glue-lined."

The problem of corrosion by ethyl alcohol almost becomes the problem of corrosion by denaturants. These at present are approximately 100 in number, and they include such diverse substances as iodine, sulphuric acid, brucine, several ketones, several aldehydes, various esters, acetic acid, many essential oils, benzene, and complex mixtures such as those obtained by the destructive oxidation of certain petroleum fractions or from certain cuts of liquids obtained by the destructive distillation of wood. The end use of alcohol determines which formula is available to the purchaser, and thus the corrosion problems incurred by users of alcohol are based very largely on the formula or formulas involved, superimposed upon the normally insignificant corrosive properties of alcohol itself. The apparatus difficulties of an ester manufacturer using alcohol denatured with sulphuric acid are quite different from those of a pharmaceutical concern which employs alcohol denatured with acetone.

Stoneware.—Chemical stoneware is impervious to ethyl alcohol at all concentrations and temperatures. The only temperature limitations are those to which chemical stoneware is normally subjected. However, because other materials of construction which are more economical and offer advantages such as weight and ease of fabrication are also impervious to ethyl alcohol, chemical stoneware is not widely used for the handling of this material. During the war, owing to scarcities of metals, chemical stoneware was sometimes used for tower sections and piping, but as these other materials became available the use of stoneware has declined. (Herstein, F. E., Chemical Stoneware, *Chem. Eng.*, Vol. 55, No. 9, p. 248, 1948.)

Carbon and Graphite.—The largest use of Karbate equipment in connection with alcohol has been in alcohol chlorination processes, and extensive tests both in the laboratory and in the field have established the excellent service life of Karbate material in these processes.

Karbate pipe and pipe fittings, globe valves, and centrifugal pumps are used in the conveying systems of various industrial processes using ethyl alcohol and its derivatives. A particularly interesting application is the use of a Karbate centrifugal pump as a mixer reactor for the production of chloral. In this application the chlorine is injected into the alcohol stream just prior to the suction of the pump, and consequently a thorough dispersion of the chlorine throughout the alcohol is obtained by the turbulent action inside the pump.

Porous carbon diffusers or perforated Karbate pipe diffusers are being used successfully in connection with alcohol chlorinating processes. Other porous carbon diffusers have found use in stripping butyl alcohol from heavier organic liquids by bubbling air through the mixture. (Revilock, J. F., Carbon and Graphite, *Chem. Eng.*, Vol. 55, No. 10, p. 236, 1948.)

Stainless Steel.—The stainless steels are widely used in applications involving alcohol, both in the industrial-alcohol field, where chemical purity of the product is essential, and in the beverage industries, where strict sanitation and cleanliness requirements must be observed. A wide number of compounds come under the classification of alcohol, but most important is ethyl alcohol, and in this field stainless steel has been satisfactory in numerous applications.

Stainless-steel grades in the 300 series (chromium-nickel) and in the 400 series (straight chromium) can handle the alcohols at almost all temperatures. Type 304 is probably most commonly used for such applications. (Renshaw, W. G., Stainless Steel, *Chem. Eng.*, Vol. 55, No. 10, p. 235, 1948.)

Aluminum.—Aluminum alloys are eminently suited for service with most of the commercial alcohols. Chemical equipment and shipping containers made of aluminum are extensively employed for industrial and beverage alcohols. Available information indicates that, at room temperature, commercial alcohols, such as methyl, ethyl, propyl, and butyl, are substantially without effect on aluminum. At elevated temperatures, aluminum is normally suitable provided a trace of moisture is present. Even those alcohols which contain heavy metals or other contaminants generally can be successfully handled in aluminum by the addition of an inhibitor, such as sodium chromate. Aluminum stills, heat exchangers, piping, tankage, and shipping containers have given long service with a variety of alcohols and products employing alcohol in their manufacture.

High-purity products, such as perfumes containing alcohols, are normally handled and shipped in aluminum bottles or other containers. An aluminum still and pipe for handling 95 per cent denatured alcohol have been in satisfactory use for over 6 years. (Balash, J. P., and E. D. Verink, Jr., Aluminum, *Chem. Eng.*, Vol. 55, No. 10, p. 240, 1948.)

Iron, Steel.—Cast iron and steel are extensively used for tanks, pumps, and pipe lines handling methyl, ethyl, butyl, amyl alcohol, glycerin, and glycols. Satisfactory equipment life can usually be expected. However, alcohol and water solutions, in the presence of air, may cause excessive corrosion, as may the presence of small amounts of organic acids. In some instances, slight contamination and discoloration may occur; high-purity glycerin, for example, is usually stored in more resistant materials when color is important. (Spitz, A. W., Iron and Steel, *Chem. Eng.*, Vol. 55, No. 10, p. 242, 1948.)

Nickel Alloys.—Nickel, Monel, and Inconel usually are highly resistant to all the alcohols, including the higher alcohols, even at elevated temperatures. The Ni-Resist alloys, with the exception of the stainless variety, Type 5, may be subject to superficial rusting in water solutions of the alcohols, but actual corrosion rates of all these alloys usually are very low. Many of the applications of nickel, Monel, and Inconel in connection with alcohols are in the preparation and handling of alcoholic mixtures such as drugs, perfumes, hospital solutions, or alcoholic beverages where it is desired to keep metallic contamination at a minimum. Other applications are in the reactions of alcohols with other chemicals, as in esterifications for such equipment as reactors, heating coils, piping, and agitators. Other applications include distilling and condensing equipment in the recovery of alcohols by distillation from or with other solvents such as acetates and acetone in solvent recovery processes. (Friend, W. Z., Nickel, Nickel Alloys, *Chem. Eng.*, Vol. 55, No. 10, p. 246, 1948.)

Tantalum.—As far as it is known, tantalum is inert to all alcohols, esters, aldehydes, and ketones at all concentrations and temperatures at which it has been tested or used. Other metals less valuable than tantalum appear to be sufficiently satisfactory, however, so that there are few, if any, applications where tantalum need be considered in corrosion problems where alcohol alone is involved.

When alcohol is mixed with acids, however, problems of corrosion or product contamination become more difficult, and sometimes the use of tantalum becomes necessary. One possible instance is where sulphuric acid is used to dehydrate alcohols. Here tantalum heaters and condensers can be used in the distillation operations and also to concentrate the acid for reuse.

In food and pharmaceutical processes, there are numerous applications where contamination, taste, or odor can be traced to attack on process equipment by alcohols mixed with acids. In practically all such instances, the use of tantalum at the correct trouble spot is an effective and permanent remedy. (Scribner, L. R., Tantalum, *Chem. Eng.*, Vol. 55, No. 10, p. 252, 1948.)

Packaging

Ethyl alcohol is shipped in steel tank cars and drums and in galvanized-iron cans. Glass jugs and bottles are also used.

ETHYLBENZENE

This chemical has been produced in large volumes as an intermediate in the production of styrene for synthetic rubber and polystyrene resins.

Production

Materials of Construction.—In the styrene plant operated by the Dow Chemical Co. at Los Angeles there are no corrosion-resistant alloys, but reliance is placed on the maintenance of anhydrous conditions to enable the handling of hydrocarbons containing hydrogen chloride in mild-steel equipment. (Smith, H. H., Los Angeles Styrene Plant, *Chem. Eng. Progress*, Vol. 43, No. 4, pp. 152–154, 1947.)

On the other hand the Germans apparently did not rely on being able to maintain anhydrous conditions. At the Chemische Werke of the I.G. Farbenindustrie at Hüls, ethylbenzene was made by the same process but a glass-lined reactor was used. All lines in contact with the reactor product were coated with a phenol-formaldehyde resin. During the period when they were unable to obtain glass-lined equipment, the Germans used acid-brick linings. (Handley, E. T., *et al.*, Synthetic Rubber Plant Chemische Werke, Hüls, U.S. Department of Commerce.)

Hastelloys B and C are resistant to the aluminum chloride-hydrogen chloride-hydrocarbon complex present in ethylbenzene reactors when some water is present. Nickel or nickel-clad steel reactors are used in some cases where some dehydration is done but not enough to be able to use steel. In some more corrosive cases nickel-clad or Monel-clad steel is used for reactor covers where in contact with vapors only.

Process.—Benzene, which is purified, and ethylene are combined in the reactors in the presence of aluminum chloride. Hydrogen chloride has been shown to be necessary as a promoter in the aluminum chloride catalyzed reaction. The alkylation product is a mixture of benzene, ethylbenzene, and polyethylbenzenes, which is washed and then fed to a train of distillation towers. (Smith, *loc. cit.*)

Benzene is taken overhead in the benzene column and returned to the reactor, and ethylbenzene, if better than 99 per cent purity, is taken overhead from the ethylbenzene still and sent to the styrene system. Diethylbenzenes are withdrawn from the bottom of this column for return to the reactor, or they may be withdrawn for sale or further processing. The reaction is carried out at the boiling point of the alkylate, about 105°C. and cooling is accomplished by vaporization of benzene from the reactor.

Granular aluminum chloride is fed continuously to the reactor by means of a variable-speed screw conveyor from a hopper.

ETHYL CELLULOSE

The handling of pure ethyl cellulose, of course, causes no problem in materials of construction. However, production does have its troubles.

Production

Materials of Construction.—In order to prevent contamination of the product and corrosion, all equipment in the ethylation plant, including treating tubs, pipe lines, pumps, purification vessels, centrifugals, and dryers, are nickel or Monel, solid or lined, or silver. When high-strength caustic (30 per cent) or high temperatures are used, nickel equipment, either solid or lined, is chosen. But in all other instances Monel is satisfactory. These include the tank and agitator feeding the centrifugals.

During the war when nickel could not be obtained, silver autoclaves were used. Because of the pressure the silver had to be backed up with a heavy shell of steel. Welding of the silver shell proved difficult but was solved by atomic hydrogen welding. It was necessary to develop a special technique for carrying out this job. Silver-lined autoclaves caused considerably more trouble than nickel-lined vessels from the standpoint of maintenance.

Process.—The process employed for making ethyl cellulose by Hercules Powder Co. when the Hopewell, Va., plant was visited by the author consisted of moistening cellulose with caustic and treating the alkali cellulose with ethyl chloride under heat and pressure. The resulting product was separated from the organic solvents and other products of the reaction, washed, purified, ground, dried, and packaged for shipment. (Integration of Chemical Plant Facilities, *Chem. & Met. Eng.*, Vol. 52, No. 9, pp. 131–132, 1945.)

Sheeted cellulose is passed through a Stern shredder and blown to a covered horizontal, Monel-lined trough, where it is moistened by a spray of caustic from plain carbon-steel tanks. Wetted material moves along in the Monel screw conveyor to the reactor. The steam-jacketed autoclaves are nickel- or silver-lined and equipped with shafts and agitators of the same metal.

Ethylation is a batch process. During the reaction cellulose and caustic compete for the ethyl group of the ethyl chloride, added to the charge, resulting in formation of ethyl cellulose, ether, alcohol, and salt.

When the processing cycle in the reactor is completed, ether and alcohol are flashed off through lead-lined scrubbing equipment and carefully scrubbed with sulphuric acid to remove low-boiling contaminants. Solvents are condensed. Low wines flowing from the condensers are collected in storage tanks. Later these solvents are fed to copper-still columns where unreacted ethyl chloride is recovered for reuse and the ether and alcohol are separated for use in ethyl chloride production.

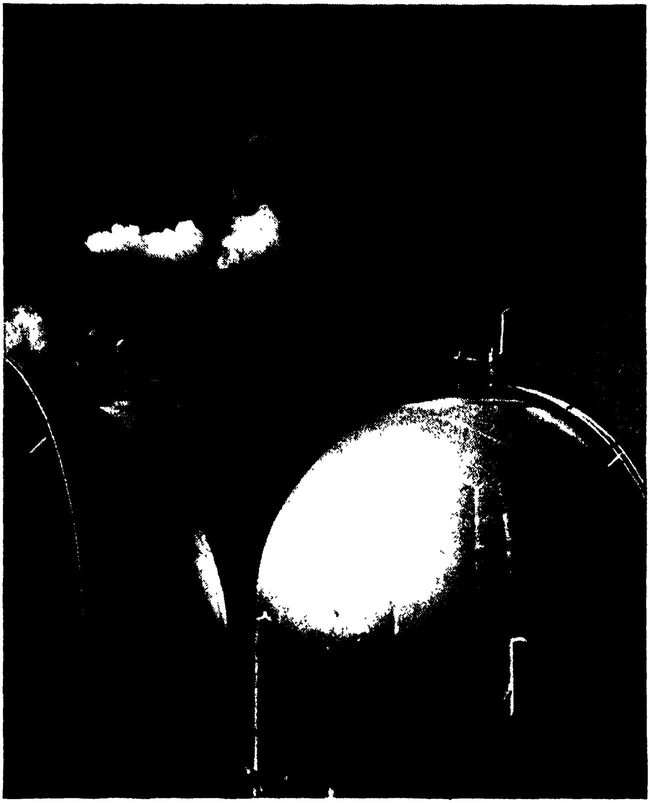
As the solvents are removed from the reactor, ethyl cellulose precipitates in a liquor consisting of caustic and brine. This slurry is blown to receiving tubs where caustic is drained off. Remaining salt is washed off.

Ethyl cellulose in granules is dropped into hammer or knife-cutter mills and ground. The ground material is dropped into wash tubs equipped with nickel-screen false bottoms where by means of water and agitation it can be washed. The product is then given a special treatment for purification.

The water slurry of purified ethyl cellulose is pumped to a Monel-lined feed tank with an agitator of the same metal. The clean product is centrifuged. The partially dried product is dumped into a bin. A dryer reduces the moisture to ½ per cent. Dried ethyl cellulose is discharged to bins.

Packaging

Granular ethyl cellulose is packed into corrugated paper cartons with an inner bag liner and having a capacity of 50 lb.



Aluminum-painted carbon steel spheroid tanks used for storing butanes at Baytown, Tex., refinery of Humble Oil & Refining Co.

ETHYL CHLORIDE

Three processes are in use at the present time for making ethyl chloride: (1) chlorination of alcohol and ether in which ethyl alcohol and ether vapors combine with hydrochloric acid in the presence of a catalyst to form ethyl chloride and water, (2) chlorination of ethylene in which ethylene gas is mixed with hydrogen chloride gas in the presence of a catalyst (the two gases first are passed through a reactor where chlorination occurs, and later through a flash drum which distils off the lighter ethyl chloride fractions leaving the heavier polymers), and (3) a process developed by Ethyl Corp.'s Baton Rouge, La., plant. This process yields ethyl chloride by reacting chlorine with waste material from one of the present ethyl chloride units and was developed to relieve the shortage of both alcohol and ethylene used in the other processes.

Production

Materials of Construction.—A high-pressure German process in which platinum plays an important role is mentioned in the literature. (Pirie, J. M., Silver and Platinum Metals in German Chemical Industry, *Chem. Ind.*, Vol. 24, No. 279, p. 231, 1948.) Ethyl chloride is cited as an example of a process in which the Germans substituted platinum for less costly materials in order to achieve a drastic economy in production costs. About 1933 a continuous high-pressure process was devised, working at 160 to 170°C. under pressure of 500 psi. in a plant containing tantalum reaction tubes and platinum-lined mild-steel autoclaves.

A plant chlorinating ethyl alcohol and ether with hydrochloric acid in the United States uses glass-lined pressure vessels and piping, porcelain, and Hastelloy B valves. Copper equipment is used for all condensing and handling operations beyond the point where acidity is scrubbed from the vapors.

Process.—In a plant of Hercules Powder Co. for the production of ethyl chloride using ethyl alcohol, ether, and hydrochloric acid the acid is stored in glass-lined steel and the solvents in steel tanks.

The acid is pumped to the building and vaporized in glass-lined equipment, mixed with ether or alcohol (each system being separate), and together fed to reaction vessels under a few atmospheres of pressure, where conversion to ethyl chloride takes place. The vaporized product leaving the reactor consists in one case of ethyl chloride and small quantities of alcohol, ethylene, water, and traces of acid and in the other case of ethyl chloride and small quantities of ether, ethylene, water, and acid. These products are passed through glass-lined scrubbing towers in order to remove acidity. They are then condensed and collected as an impure mixed solvent for transfer to the solvents-separation building. Here they are fed in the one case to the ether still column and in the other case to the alcohol column for separation of the ethyl chloride from the unreacted components. The ethyl chloride is transferred to storage tanks.

Handling

Ethyl chloride can be handled in ordinary mild steel.

Nickel-clad steel weigh tanks and Monel valves, gages, and fittings are used.

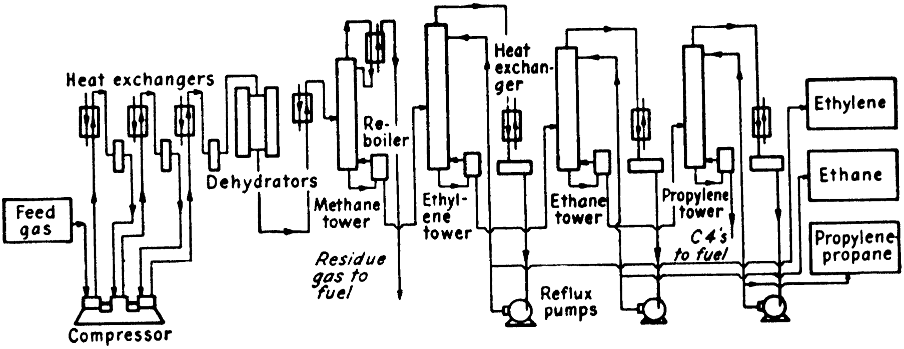
ETHYLENE

Ethylene is produced in company with many different and complex compounds, either as by-product or end product of cracking reactions from heavier hydrocarbons in petroleum, the fuel, or as component of coke-oven or manufactured gas during the dry distillation of coal. (Kniel, L., and W. H. Slager, Ethylene Purification by Absorption Process, *Chem. Eng. Progress*, Vol. 43, No. 7, pp.

335–342, 1947.) As by-product it is usually rejected in the off-gas from thermal or catalytic cracking units. Where refinery off-gas is not available or available only in insufficient volume, the pyrolysis of ethane, propane, or selected petroleum fractions furnishes large volumes of gas rich in this constituent. Irrespective of its source, product recovery from such gases presents a problem of considerable importance in the field of modern synthesis.

Production

Materials of Construction.—The Los Angeles ethylene plant operated by Dow Chemical Co. is constructed of mild steel, with the exception of the top section of the methane tower and its related equipment. (Smith, H. H., Los Angeles Styrene Plant, *Chem. Eng. Progress*, Vol. 43, No. 4, pp. 152–154, 1947.) Nickel steel, 3½ per cent, is used in these locations to assure adequate impact strengths at reduced temperatures.



Ethylene. This plant is constructed of mild steel, with the exception of the top section of the methane tower and its related equipment. Nickel steel, 3½ per cent, was used in these locations to assure adequate impact strength at reduced temperatures.

Process.—Feed gas enters the plant and is compressed to 525 lb. gage, cooled, and dried before entering the distillation system. Gases lighter than ethylene go overhead from the methane tower to fuel. This tower operates with an overhead temperature of 130°F. below zero. The bottoms from this tower are fed to the ethylene tower, which gives an overhead product of up to 97 per cent ethylene, which is sent to the ethylbenzene plant.

Bottoms of the ethylene tower are, in turn, fed to other towers.

Handling

Ethylene can be handled in ordinary materials of construction.

Packaging

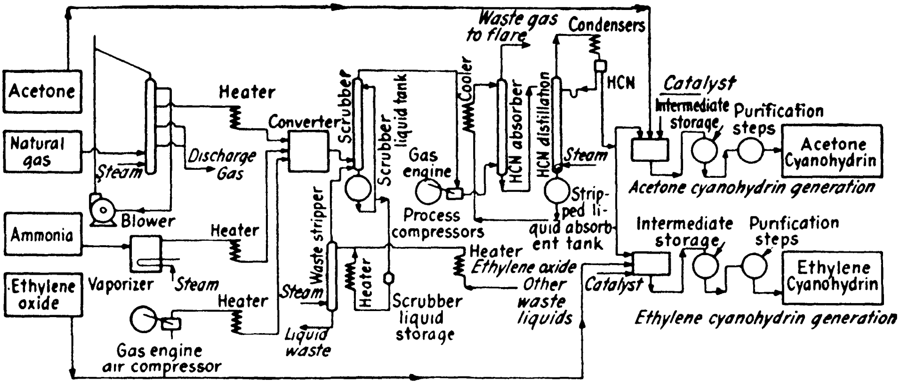
Steel is ordinarily used for shipping containers for this product.

ETHYLENE CHLORHYDRIN

This chemical was prepared at Anorgana G.M.B.H. Werk Gendorf in Germany by the action of chlorine, water, and ethylene. Ethylene was fed to the side of the reactor and chlorine at points above and below the ethylene. The reactor was cast iron, brick-lined. The condenser-scrubber was made of the same materials.

ETHYLENE CYANOHYDRIN

Ethylene cyanohydrin is used as an intermediate in the production of acrylic resins and other products. At Deer Park, Tex., Rohm & Haas Co. is producing both ethylene and acetone cyanohydrins from hydrocyanic acid. This is made in the plant from ammonia, air, and natural gas. (Lee, J. A., Hydrogen Cyanide Production, *Chem. Eng.*, Vol. 56, No. 2, pp. 134–136, 1949.)



Ethylene cyanohydrin. For HCN Type 316 stainless steel is used for towers and piping for handling moderately corrosive materials. Type 304 stainless is used where there is practically no corrosion, but where it is necessary to avoid contamination. Types 309 and 310 are used for high temperatures. Worthite and Durimet 20 are used for pumps and valves throughout the plant. Lead is used where sulphuric acid is present. Both cyanohydrins are made with plain steel, except for a few pieces of stainless steel.

Production

Materials of Construction.—Both intermediates are made with plain steel equipment, except for a few pieces of equipment which are constructed of stainless steel. For the materials of construction used in making the hydrogen cyanide see Hydrocyanic Acid.

Process.—The hydrogen cyanide is treated in a generator with ethylene oxide and a catalyst. The cyanohydrin formed is pumped to storage and is next passed through purification stages before shipment.

ETHYLENE DIAMINE

This product was made by the Germans, it is reported (Adams, D. A. W., and W. Baird, Some Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce), by liquid-phase reaction of ethylene dichloride and ammonia under pressure.

Production

Materials of Construction.—Steel was used for the columns. However, corrosion in these columns was troublesome, and 18-8 stainless steel was considered to be a more suitable material for their construction. Steel also was used for several kettles. The evaporator was made of stainless steel.

Process.—Ammonia and ethylene dichloride are mixed together in a pump and passed through a series of five ring-packed columns. The columns are of normal high-pressure steel. The reaction mixture passes from the high-pressure reactor to a steel kettle, where the bulk of the excess ammonia is distilled off to a brine-cooled receiver for reuse. Circulation of the contents of this vessel is induced by thermal means. The residual mixture of amines and amine salts, still containing a little ammonia, flows to a steel kettle at normal pressure, where the requisite amount of caustic liquor is added to liberate the free bases. This kettle carries a column half packed with raschig rings, and here the residual ammonia is stripped out. The condensate returns to the kettle, and the ammonia passes to a gasometer from which it is compressed and returned to the system.

The liquid flows from this kettle continuously to a stainless-steel evaporator in which circulation is effected by thermal means. Here aqueous 20 per cent ethylene diamine is distilled off. The salt which separates is run out periodically from the bottom of the kettle to a centrifuge.

The concentrated amines are then distilled in a stirred steel kettle carrying a fractionating column where concentrated diamine is distilled off up to 120°C. Vacuum is then applied, and crude diethylene triamine is taken off, then crude triethylene tetramine. The crude diamine is fractionated through a 30 to 40 bubble-plate column to give approximately 78 per cent strength diamine; the 20 per cent aqueous diamine is likewise fractionated through a similar column. The crude diethylene triamine and triethylene tetramine are also purified by fractionation through a column packed with iron raschig rings.

ETHYLENE DICHLORIDE

Ethylene dichloride is noncorrosive at normal atmospheric temperatures when dry (moisture-free). Iron and steel are suitable metals for storage tanks. In contact with water at elevated temperatures ethylene dichloride corrodes iron and certain other metals. (Manufacturing Chemists Association, "Ethylene Dichloride," Chemical Safety Data Sheets SD-18.)

Nickel-clad steel and Monel are used for distillation equipment and condensers for recovery of ethylene dichloride where used in solvent extraction.

Packaging

This chemical can be shipped in wooden boxes or fiber boxes with inside containers. Metal drums and tank cars can also be used.

ETHYLENEIMINE

A British team of engineers visiting Germany after the Second World War found that ethyleneimine was being produced by the I.G. Farben. at Ludwigshafen. (Adams, D. A. W., and W. Baird, Some Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.)

Production

Materials of Construction.—Zinc-lined casks were used for holding the hydrochloride. However, corrosion was so severe that these casks could be used only once. When a larger plant is built, chemical stoneware or glass-lined steel tanks will be provided.

Stoneware was used for melting the amine hydrochloride. Most of the remaining equipment was made of ordinary iron and steel.

Process.—Production of ethyleneimine starts with the neutralization of ethanolamine with dry hydrochloric acid. The hydrochloride is run molten to zinc-lined casks. The amine hydrochloride is charged to a covered, shallow, jacketed, stoneware basin carrying a very powerful stirrer, where it is melted at 70 to 80°C. Thionyl chloride is run in slowly during 8 to 10 hr. with cooling. Liberated gases pass to an absorption system. The reaction mixture is initially liquid and gradually becomes more viscous; it finally solidifies and is broken up by the stirrer. The cover of the pan is then lifted, and the product transferred by shovels to casks.

The chlorethylamine hydrochloride is dissolved in water in an iron kettle, and 40°Bé. caustic liquor added together with further water to give a 15 per cent concentration of caustic soda. The charge is then heated to the boiling point, and the ethyleneimine distilled off. The distillate is dried over caustic, and the ethyleneimine layer redistilled. The product is stored in iron containers over caustic and cooled in solid carbon dioxide to prevent spontaneous polymerization.

ETHYLENE OXIDE

It has been reported that ethylene oxide was made by the German I.G. Farbenindustrie at Gendorf. (Adams, D. A. W., and W. Baird, Some Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.)

Production

Materials of Construction.—The tower is packed with porcelain rings. For handling chlorohydrin, porcelain or Haveg pipe was used. Ethylene oxide is stored in mild steel. (*Ibid.*)

Pipe lines in this plant are usually mild steel. Valves are usually by contrast stainless steel. The plant chemist was in favor of having stainless pipe as well as valves. (Notes of Manufacturing of Ethylene Oxide, Final Report 360, Item 22, British Intelligence Objectives Sub-Committee, His Majesty's Stationery Office, London.)

Process.—The chlorohydrin tower is packed with 50- to 70-mm. porcelain raschig rings. The gas distributors are of Haveg. In the chlorohydrin tower, water is fed at 10 to 15° to the bottom of the tower, the chlorine inlet is about 1 m. above this, and the ethylene inlet a further 1 m. higher. The chlorine is fed in as gas at about 2 atm. pressure (not less than 1.8 atm.) via a meter, the rate being about 1,150 to 1,200 kg. per hr. It is important that the rate should be steady and that no chlorine is present in the off gases from the top of the reactor. Ethylene of 95 per cent purity and at 1.1 atm. pressure is first cooled to below 30°C. by circulating with water through a pump, the water in turn being circulated through a cooler. The ethylene feed rate (also metered) is about 500 cu. m. per hr. Water should be adjusted to give a chlorohydrin content of 4.5 to 4.7 per cent. There is also a relatively small addition of water in the form of a spray at the top of the tower to wash the exit gases. (Adams and Baird, *loc. cit.*)

The gas residues at the top of the tower are at about 40 to 80 cm. water pressure and contain approximately 15 to 20 per cent ethylene, 2 to 3 per cent ethane, 1 per cent acetylene, 1 per cent nitrogen, and 0.5 per cent carbon dioxide arising from the ethylene feed. This gas passes through a caustic scrubber, and one-third is returned to the ethylene feed and the remainder blown to atmosphere.

The chlorohydrin liquor flows from the top of the reactor at a temperature of 45 to 50°C. This is determined primarily by the initial water temperature, but an exit temperature about 50°C. leads to the presence of too much water in the off-gas. When starting up the reactor, it is the practice to reduce the water feed until the exit temperature reaches 45 to 50°C. and then to adjust to the correct chlorohydrin concentration while maintaining this temperature limit.

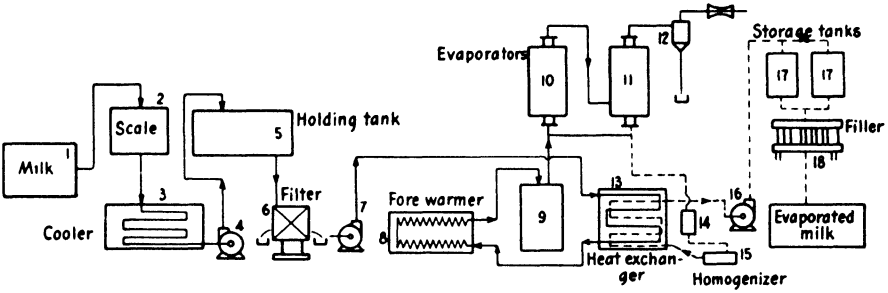
The chlorohydrin liquid is fed via a porcelain or Haveg pipe to the saponifiers, 10 per cent milk of lime being fed at 80°C. Steam is fed to the saponifiers. The effluent calcium-containing liquor should contain free calcium hydroxide. This is usually around 1.5 per cent, but with very carefully controlled operation it can be reduced to about 0.5 per cent.

Vapors from the saponifier pass through a dephlegmator at 60°C. and thence via a cooler at 30°C. to the first distillation column. The temperature of the first boiler is maintained at 80 to 82°C. with the column head at 12°C.; in the second column the temperatures are 45 to 50 and 12°C., respectively. The ethylene oxide from the first column is about 97 per cent pure and from the second 99 per cent or higher. An atmosphere of nitrogen is maintained in the distillation apparatus.

The ethylene oxide is stored in mild-steel tanks cooled to −14°C., with an internal coil carrying glycol as cooling medium. The liquid content is measured using a steel-tipped floater in a nonmagnetic steel tube with a sliding magnetic pointer. A nitrogen pressure of about 1.5 atm. is maintained on the tanks, and liquid ethylene oxide is pumped to wherever it is required. The pump has a carbon packing—an asbestos packing was actually in use but was less satisfactory—and the gland is cooled with glycol at −14°C.

EVAPORATED MILK

Strict regulations demand cleanliness in the preparation and handling of evaporated milk. This, in turn, calls for special materials of construction.



Evaporated milk.

1. Tinned steel
2. Stainless steel
3. Stainless steel
4. Stainless steel
5. Glass-lined, stainless
6. Stainless steel
7. Stainless steel
8. Stainless steel
9. Stainless steel, glass-lined
10. Stainless steel
11. Stainless steel
12. Carbon steel
13. Stainless steel
14. Stainless steel
15. Stainless steel
16. Stainless steel
17. Stainless steel, glass-lined
18. Stainless steel

Production

Materials of Construction.—Stainless steel is used for many of the essential pieces of equipment which come into contact with the milk. Where weight is no objection, as in the case of holding tanks, glass-lined steel is used. Other equipment is ordinary carbon steel. A large number of horizontal tanks are used for holding milk prior to processing.

Process.—Raw milk is delivered to the plant in trucks in both cans and tank-load lots. Stainless-steel pipe and fittings and sanitary pumps are used to unload tank trucks. Milk is pumped to glass-lined steel or stainless-steel holding tanks.

Milk from storage at 36°F. is passed through a filter to a regenerative plate heater and cooler. (McCarthy, F. W., Advance Engineering in Processing Evaporated Milk, *Food Ind.*, Vol. 20, pp. 1594–1597, 1948.) As is now almost universal, these heat exchangers are made entirely of stainless steel.

The raw milk leaves the heater at 100°F. and is pumped to a forewarmer which raises the temperature to 190 to 210°F. It passes to a hot well for 20 min. A two-stage stainless-steel vacuum evaporator reduces the moisture content by 80 per cent. Milk leaves the second effect at 120°F. and falls into a stainless-steel or glass surge tank feeding the stainless homogenizer. The latter forces the milk through the regenerative plate exchanger. The temperature is lowered to 38°, and the milk goes to stainless-steel or glass-lined storage tanks. It is then canned.

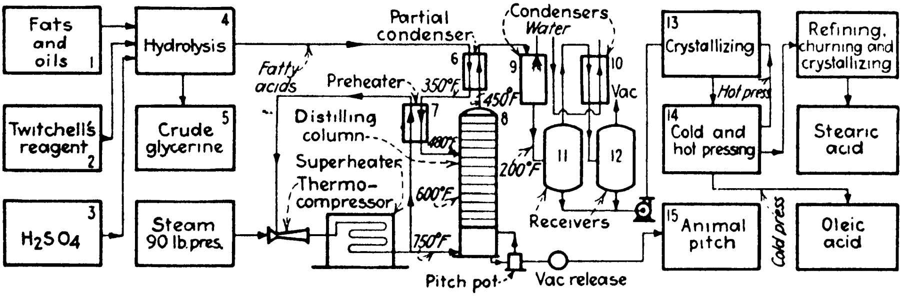
FATTY ACIDS

Fatty acids may be of either vegetable or animal origin. They may be used separately or mixed in subsequent operations. They do not occur in a free state, but as complex fatty oils, consisting principally of glycerides of the organic fatty acids. The term "fatty acids" is used here to cover acids of higher molecular weights, such as oleic.

Production

Materials of Construction.—Recent installations of fatty-acid equipment have made extensive use of stainless steel, stainless-clad steel, aluminum, nickel, and Monel. This has been particularly true in the case of stills, condensers, separators, and pipe lines.

There is a trend away from the use of copper and high-copper alloys, especially in the final processing of soap, where possible contamination of the product with



Note: For details of hydrolysis, separation of acids and final purification see flowsheet, Chem. and Met., p. 340, June, 1934 (Vol. 34)
Steam (750 deg F.), 0.695 lb. per lb stock charged; recovery efficiency, 90 percent plus. Chart based on fatty acids of about 25 percent palmitic, 25 percent stearic, 50 percent oleic

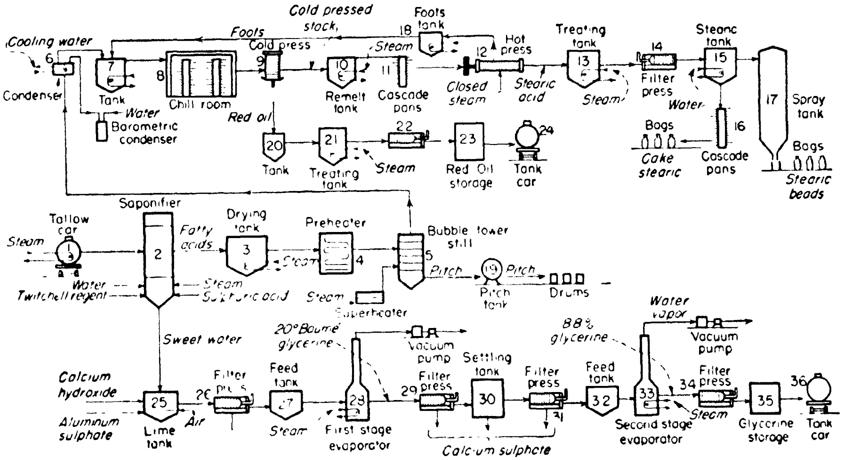
Continuous fatty-acid refining (Goranflo process).

1. Steel
2. Steel
3. Lead-lined steel
4. Monel
5. Steel
6. Aluminum
7. Monel
8. Stainless steel
9. Aluminum
10. Aluminum
11. Aluminum
12. Aluminum
13. Aluminum
14. Steel and aluminum
15. Cast iron

copper compounds is considered objectionable. However, copper is still used to some extent for bubble towers in stills for crude fatty acids.

The fats which are used as the raw materials for fatty acids are shipped and stored in steel, which considering costs and availability is probably the most satisfactory construction material. From the storage tanks the fats pass to acid (sulphuric) washing tanks which are lead-lined steel or wood. Some concerns prefer steel tanks; others wood with lead linings. Both types have given complete satisfaction. No other lining materials have proved so satisfactory as lead.

This, however, is not true of the saponifying tanks, which also employ copper linings. These tanks are either of wood or of steel, lined with lead, Monel, or copper. Although they are more expensive, copper-lined tanks have been found to last longer. Still other companies believe it preferable to use unlined cypress tanks, replacing them as frequently as need be. It is true that they do not last so long as lined tanks, but there seems to be considerable question as to the economies involved. In any case of unlined tanks it is to be noted that only



Stearic acid, red oil, and glycerin.

1. Steel
2. Monel
3. Steel
4. Stainless steel
5. Inconel
6. Aluminum
7. Aluminum
8. Stainless steel
9. Steel with aluminum plates
10. Aluminum
11. Stainless steel
12. Steel
13. Monel
14. Aluminum
15. Aluminum
16. Aluminum
17. Aluminum
18. Aluminum
19. Steel
20. Aluminum
21. Monel
22. Aluminum
23. Aluminum
24. Aluminum
25. Monel
26. Cast iron
27. Steel
28. Steel
29. Cast iron
30. Steel
31. Cast iron
32. Steel
33. Steel
34. Cast iron
35. Steel
36. Steel

the best grade of cypress is worth using. The most recent installations have been fabricated from Type 316 stainless steel, Monel, or nickel. When the fats are hydrolyzed in an autoclave, copper and more recently stainless steel, nickel, or nickel-clad steel have been used.

In the continuous, concurrent process Inconel or Type 316 stainless steel is used. In the continuous, countercurrent process the hydrolyzer is a stainless-steel column and the equipment throughout the process is made of stainless steel where the fatty acids are at high pressure or temperature but of aluminum where at low pressure.

Filter presses are employed for a number of purposes. For the sweet water, ordinary cast-iron plates are suitable, while for the fatty acids, an aluminum and silicon alloy has performed satisfactorily. Tin-covered copper for this purpose requires frequent retinning and is not considered satisfactory.

Evaporators of cast iron with copper tubes are very long-lived. It is possible, however, that other types may be preferable. Stills for many years have been built of cast iron, but more recently, other metals such as stainless-clad steel, stainless steel, aluminum, copper, Monel, nickel, and Inconel have been introduced. Very rarely do cast-iron stills fail by being eaten away. Failure is generally by cracking.

Copper has been used for many years and with complete success for condensers, although in recent years aluminum, stainless steel, stainless-clad steel, nickel, and Monel also have been used.

Three materials are used for the slab pans: enameled iron, stainless steel, and aluminum. The last is best but more expensive, so that enameled pans are generally used for the crude acid and aluminum for the finished product.

Both cold and hot presses are made of ordinary steel or iron. As far as is known, other materials have not been employed for this purpose.

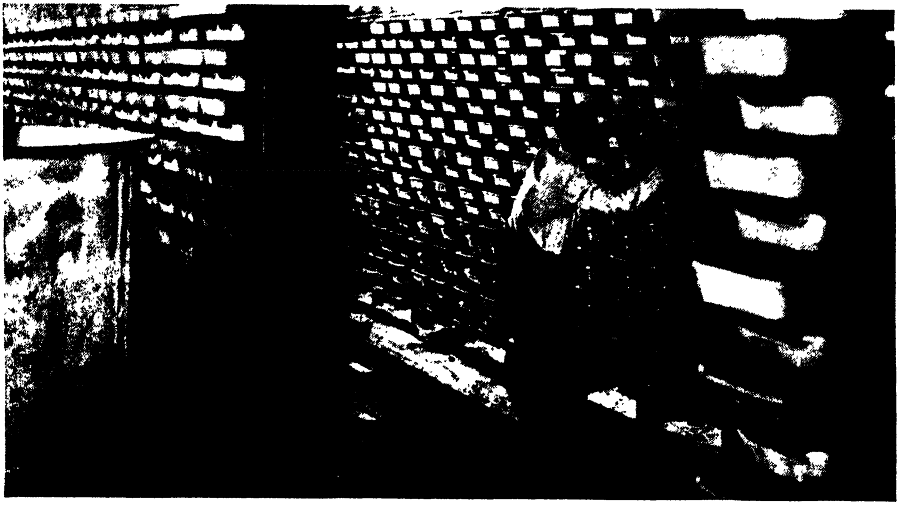
For remelting the acid cake, aluminum or either unlined cypress or wood tanks or steel tanks, lead-lined, are used. There are engineers who contend that unlined cypress is fully satisfactory, and it is certainly cheaper. The same situation holds in the case of the churns, where both lined and unlined tanks have been found suitable.

Red brass, bronze, copper, aluminum, steel, wrought iron, stainless steel, Durimet 20, stainless-clad steel, nickel, and Monel are among the materials used for piping and pumps. Both centrifugal and ordinary steam pumps are met, bronze being the most suitable material for the stock end. Aluminum pipe is probably the best in that it seems to have the least effect on the stock, although brass and copper both have proved very satisfactory.

Strangely enough, however, none of these metals seems to have worked out as a thoroughly satisfactory solution to the valve problem. Brass gate valves appear to be most used and, although the cause of considerable trouble, are generally thought to be as good as anything obtainable. Replaceable seats and gates are said to be worth-while economy. Teflon seating disks have been used in globe valves and needle valves with excellent results, since they resist erosion as well as corrosion in fatty acids at 400°F.

Fatty acids can be safely stored in aluminum, nickel-clad steel, nickel, stainless steel, stainless-clad steel, cypress, cast iron, or plain steel, depending on the purpose.

The successful application of aluminum depends to a large extent upon the inorganic impurities carried in by the raw stock or picked up as metallic compounds from other equipment. The pickup of compounds of some heavy metals, such as lead, copper, and nickel, especially when chlorides are present, has caused corrosion of aluminum equipment used to process fatty acids. The purified fatty acids at elevated temperatures can be corrosive to aluminum unless there is a trace of water present, the water acting as a very effective inhibitor for the corrosion of aluminum alloys by the fatty acids at high temperatures. Equipment such as filter presses, stills, condensers, piping, spray tanks, refined-oil tanks, red oil tanks, crude-oil tanks, and cascade pans constructed of aluminum have given good service.



Fatty acids in aluminum pans are solidified in a chill room. Application of aluminum depends to a large extent upon impurities carried in by raw stock or picked up as metallic compounds from other equipment.

Processing.—In this country most of the commercial fatty acids are obtained by the "splitting," or hydrolysis, of naturally occurring fats and oils without the use of alkali. The important general methods for accomplishing this splitting are the Twitchell and autoclave processes (both of which are batch) and the continuous splitting process. (Marsel, C. J., and H. D. Allen, Fatty Acid Processing, *Chem. Eng.*, Vol. 54, No. 6, pp. 104–108, 1947.)

Twitchell Process.—This process is the simplest method of fat splitting. The operation is carried out in tanks, where the acid-washed fat is mixed with 25 to 50 per cent water and 0.75 to 1.25 per cent catalyst. Hydrolysis is accomplished by boiling with open steam for 20 to 48 hr. Considerable amounts of albuminous material and other impurities present in poorer stocks usually necessitate preliminary acid refining with strong sulphuric acid. The splitting is carried out in two to four stages, the "sweet water" (glycerin solution) being withdrawn at the end of each stage and replaced with fresh water or weaker sweet water from a previous boil. (*Ibid.*)

Autoclave Process.—High-pressure autoclave splitting is the oldest nonalkaline commercial process. Autoclaves are about 4 to 6 ft. in diameter and 20 to 40 ft. high. After charging with fat, catalyst, and 30 to 60 per cent water, steam is admitted to reach the desired pressure. Upon splitting, the contents are blown to a separating tank, where the fatty acids are drawn off from the sweet water. The catalyst must be removed by acid treatment. (*Ibid.*)

Autoclave fat splitting without catalyst is not used widely. A stainless-steel autoclave with mechanical agitation gives rapid splitting at 450°F. with the production of light-colored fatty acids, and a pure glycerin solution, providing a good grade of raw stock is used.

Continuous Countercurrent Process.—The process which bids fair to dominate future developments in the field is continuous, countercurrent, high-pressure, high-temperature splitting. The concept of continuous hydrolysis is by no means a new one; however, commercial development was not forthcoming until high-pressure equipment of acid-resistant stainless-steel alloys became easily available. (*Ibid.*)

Fatty oil is passed through a vacuum deaerator (to prevent darkening by oxidation during processing) and then fed at a controlled rate to the bottom of the hydrolyzing tower built of Type 316 stainless steel. Here the oil contacts the aqueous glycerin leaving the column and, rising because of its lower density, extracts the small amount of fatty material dissolved in the aqueous phase. At the same time deaerated and, in hard-water areas, demineralized water is fed to the top of the tower. Here it flows down over trays in contact with the upward-flowing split acids and extracts from them the glycerin dissolved in the fatty phase. After leaving the contacting sections of the tower, the two streams are brought to reaction temperature by direct injection of high-pressure steam; they then enter the main reaction zone where the final phases of the splitting occur. This process can be operated catalytically, the usual catalysts being zinc, magnesium, or calcium oxides. Naturally, during the process the actual catalysts would then be the fatty-acid soaps of the corresponding heavy metal.

The fatty acids, upon discharge from the top of the tower, flow to a decanter where the water still suspended in them is separated. An interfacial level controller in the splitting column maintains the position of the interface between the fatty phase and the aqueous phase by regulating the discharge of the aqueous glycerin to the glycerin storage tank.

Concurrent Process.—Mention should be made of the Eisenlohr process (Schwitzer, M. K., Modern Trends in Fat Splitting, *Chem. Age,* pp. 601–606, June, 1944; and Marsel and Allen, *loc. cit.*), in which the flow of oil and water is concurrent rather than countercurrent. Oil and water are emulsified and passed into reaction coils, where splitting is rapidly accomplished at 600°F. and 3,500 psi. The reaction mixture of water, glycerin, and fatty acids is released into a flash chamber, where a substantial part of the water evaporates. The remaining mixture is cooled and settled to afford separation of fatty acids from the 35 per cent glycerin solution.

Purification.—In most cases, it is desirable to purify the acids following the splitting, although this choice depends on the original quality of the raw stock and the use intended for the fatty acids. The usual method of purification is vacuum distillation of the acids, although recent developments indicate that solvent extraction may also give the desired purification. (Anon., Refining Vegetable Oils by Petroleum Methods, *Chem. Eng.*, Vol. 53, No. 12, p. 120, 1946; and Marcel and Allen, *loc. cit.*)

Vacuum distillation is usually carried out with the aid of stripping steam. This step allows the distillation to proceed at a lower temperature but requires the use of larger equipment in order to avoid excessive pressure drop through the condensing system as compared with an equivalent amount of fatty acid distilled without steam. The ordinary distilling temperature is from 450 to 500°F., with maximum permissible temperature depending principally on the degree of unsaturation of the acids; a highly unsaturated stock (as linseed oil fatty acids) undergoes excessive polymerization at higher temperatures. Another factor to be considered in distillation is the extreme corrosiveness of hot fatty acids, which necessitates the use of special high-chrome-nickel stainless steel such as Type 347 for equipment construction.

Packaging

Aluminum tank cars are used for shipping fatty acids.

FERRIC CHLORIDE

This is one of the difficult chemicals from a corrosion viewpoint. The hydrochloric acid associated with ferric chloride in production and handling is the troublemaker.

Production

Materials of Construction.—In the case of the anhydrous product plain iron and steel equipment are sufficient. The situation when moisture is present is more complex. Rubber, stoneware, Hastelloy C, high-silicon iron, and Karbate are used for the aqueous material. Pyroflex with fused-on ceramic lining in a steel outer shell is now handling the treatment of scrap iron with hydrochloric acid or chlorine at 266°F. (Rauh, C. A., Pyroflex Constructions for Acid and Alkali Service, *Trans. A.I.Ch.E.*, Vol. 35, p. 463, 1939.)

Process.—The aqueous product can be made by trickling water over scrap iron in an acid-resistant tower. Chlorine gas enters the tower at the bottom and passes up through the iron and water. The ferrous chloride solution thus formed is next chlorinated in an acid-resistant tank to ferric chloride.

Handling

Of the metallic materials, Hastelloy C is among the most resistant to ferric chloride. It is in use where oxidizing agents such as ferric chloride are present. It is believed that position welding of Hastelloy pipe in the field was utilized for the first time with ferric chloride installations. (Schrader, R. J., and A. DeHaan, Special Materials Solved Corrosion Problems at Oak Ridge, *Chem. Eng.*, Vol. 53, No. 11, pp. 96–101, 1946.)

Some high-silicon iron pumps are said to be in use for handling and producing ferric chloride. Durimet 20 is not recommended, nor are most of the other metals and alloys.

Hard rubber is in use. Special soft-rubber compounds can handle the chloride solutions up to saturation at 150°F.

Karbate can handle solutions up to the boiling point. Chemical stoneware also is used. Saran-lined steel pipe is used for concentrated ferric chloride solutions at 15 to 40°C. Phenolic and vinyl copolymer protective coatings can be used.

FLUORIDES—SULPHURIC ACID

Carbon, graphite, and Karbate materials have proved satisfactory for service with mixtures of sulphuric acid and fluorides. (W. W. Palmquist, Carbon and Graphite, *Chem. Eng.*, Vol. 55, No. 6, p. 226, 1948.)

FLUORINE

Fluorine, like chlorine, is not a difficult chemical to work with when dry but one of the most troublesome when wet. Although it is still a comparatively recent commercial chemical, much knowledge has been gained about materials suitable for its production, handling, and packaging.

Production

Materials of Construction.—For the most part materials of construction that are suitable for the handling of wet and dry fluorine, aqueous and anhydrous hydrofluoric acid, and their mixtures can safely be used in production of fluorine.

Process.—Several electrolytic cells of the diaphragm type have been developed and put in operation for the production of fluorine. Ordinary carbon steel is suitable for the principal parts of the cells, including the cell body, water jacket, hydrofluoric acid feed line, cathode, and solid parts of the diaphragm. In one case a Monel screen is used to separate the anode and cathode compartments. The electrolytes vary. The Pennsalt cell uses a solution of anhydrous hydrofluoric acid in fused potassium fluoride and hydrogen fluoride, and the Harshaw electrolyte is fused $KF \cdot 2HF$ with 1 to 1.5 per cent lithium fluoride as an additive.

Fluorine is purified by removing the hydrofluoric acid either by absorbing it in sodium fluoride or by chilling. After purification, the fluorine gas is used directly or is compressed and put into steel, nickel, or Monel cylinders for storing or shipping. The last two are recommended for maximum safety.

Handling

Nickel and Monel show good resistance to fluorine at temperatures up to 450°C. Carbon steels with less than approximately 0.01 per cent silicon are resistant up to 350°C., but corrosion increases rapidly with increased silicon content. The stainless steels, with the exception of Type 347, show satisfactory resistance up to 250°C.; aluminum and magnesium are resistant up to 450 and 300°C., respectively; corrosion of these materials is not great even above these temperatures. Copper was found to be unsatisfactory for handling fluorine at elevated temperatures, but the oxygen content of the fluorine used may have caused the very high rates. (Myers, W. R., and W. B. DeLong, Fluorine Corrosion, *Chem. Eng. Progress,* Vol. 44, No. 5, p. 359, 1948.)

None of the stainless steels tested is suitable for handling fluorine above 250°C. Type 347 showed a high rate at even this temperature. It is probable that the volatile columbium pentafluoride is responsible for the high rate obtained on Type 347, but it is not clear why Type 309 Cb did not behave similarly. The presence of silicon is probably responsible in part for the poor resistance of the stainless steels. The wrought stainless alloys normally contain approximately 0.5 per cent silicon.

Fluorine gas can be conducted in steel pipe or copper tubing at atmospheric temperature without noticeable attack except for the formation of white scale on the interior surface and some corrosion at the exit end of the pipe where it is exposed to atmospheric moisture. In pipes which are subject to flexure or vibrations, the protective fluoride deposit may flake or powder off and the resultant scale may accumulate in restricted parts of the line. In the case of iron pipe, oxide scale sometimes present in new pipe will be converted to a powdered fluoride, which may similarly cause line stoppages. If a section of iron pipe is locally heated, *e.g.*, by combination of dirt or grease in the joints, continued combustion may ensue, and a substantial portion of the pipe may be destroyed if the passage of fluorine is continued. For applications where the formation of fluoride scale is undesirable or where elevated temperatures may be encountered, Monel or nickel pipe is recommended. (Gall, J. F., and H. C. Miller, Small Scale Production and Handling of Fluorine, *Ind. Eng. Chem.*, Vol. 39, No. 3, p. 262, 1947.)

In view of the fact that Monel or nickel pipe is much more resistant to ignition by fluorine than is steel, the use of Monel or nickel for piping is preferable for the handling of pure fluorine, particularly under pressure. (Landau, R., and R. Rosen, Industrial Handling of Fluorine, *Ind. Eng. Chem.*, Vol. 39, No. 3, p. 281, 1947.)

Experience has shown that welded construction is preferable to either flanged or screwed piping at any pressure, since leakage or contamination which may result in fire may occur with the latter. Where joints are necessary for repairs or other operating purposes, a flanged joint is preferable, but the gaskets must be limited to metals, such as soft copper or aluminum rings, or inert plastic rings, *e.g.*, Teflon (polytetrafluoroethylene), for the low pressures. For dilute gases (below 20 per cent) clean butyl or neoprene gaskets can be used, provided the surface of contact with gas is comparatively small and the joint is not broken frequently. Most rubbers, except butyl, lose their physical strength quickly on exposure to fluorine, so that it is desirable to replace the rubber gasket each time the joint is made up. A copper-jacketed asbestos gasket can also be employed for dilute gases. (*Ibid.*)

Because of the abrasing action encountered in the turning of a valve, materials which show minimum scale formation are preferred for valve stem and seat, and Monel and nickel are preferred. For the same reason, globe- or needle-type valves are preferred to gate valves, and plug cocks are found to be definitely unsatisfactory. For use with fluorine at atmospheric pressure, Teflon packing works well, provided the bulk-surface relations in the packing are such that thermal release is good in the event of incipient combustion of the packing. Diaphragm, bellows, and other types of packless valves are satisfactory if the operating mechanism in contact with the fluorine is not readily made inoperative by fluoride scale. (Gall and Rosen, *loc. cit.*)

Packaging

Fluorine gas is compressed and put into steel, nickel, or Monel cylinders for shipping. The last two are recommended for maximum safety.

FLUOROLUBES

The fluorolubes are addition polymers of trifluorovinyl chloride. In process of manufacture the polymers are stabilized by subjection to rigorous fluorination conditions. Terminal groups are fluorinated, and any loosely held chlorine in the chain is replaced by fluorine.

The fluorolubes are stable chemically, being inert to liquid oxygen, high-strength hydrogen peroxide, chlorine, etc.

Handling

They are relatively noncorrosive to the common metals.

Since they are very heavy and relatively expensive, these lubricants are being shipped in lead-lined pails only for the purpose of preventing any outside contamination or discoloration.

FORMALDEHYDE

The modern formalin plant is comparatively simple in general arrangements, and the chemical engineering problems are mostly concerned with corrosion. Formaldehyde itself is chemically very active, but most of the corrosion is caused by traces of formic acid which are always present. (Homer, H. W., *J. Soc. Chem. Ind.*, Vol. 60, No. 8, pp. 213–218, 1941.)

Production

Materials of Construction.—Stainless steels are looked upon with greatest favor for use with formaldehyde. The McCarthy Chemical Co.'s plant uses stainless steels for the fractionating towers and other equipment which comes into contact with this chemical. (Hightower, J. V., Organics from Natural Gas, *Chem. Eng.*, Vol. 56, No. 1, pp. 92–94, 1949.)

Aluminum alloys have been widely used in equipment for production of formaldehyde. This chemical does promote pitting of aluminum, which is most apparent shortly after the equipment is placed in service. However, apparently this rate decreases markedly with time and, as a result, becomes self-limiting. For example, a still was placed in service some 18 months ago. After 6 months' use the attack appeared to be severe. However, after 18 years' service this piece of equipment is still in service and functioning satisfactorily without any repairs being needed because of corrosion. Unless appearance is a criterion of utility, aluminum will be satisfactory for many pieces of equipment producing formaldehyde. Aluminum alloys have been used in this country for the construction of reaction chambers, stills, condensers, storage tanks, and piping. An interesting application is the transport of formaldehyde.

At the Leverkusen plant of the I.G. Farben. aluminum is used for most of the equipment. (Clough, H., Manufacturing of Formaldehyde at I.G. Farben., B.I.O.S. Final Report 1788, Item 22, British Intelligence Objectives Sub-Committee, His Majesty's Stationery Office, London.) Apart from the evaporator tubes and tube plates, which are 18-8 stainless steel, the evaporator is fabricated from tinned copper; ferrous materials are to be avoided as far as possible to minimize transfer of iron to the catalyst bed.

In the converter is the silver catalyst supported on a copper gauze. Grids supporting the copper are machined from a heat-resisting nickel-chromium steel. The catalyst grid is supported inside the converter proper by a pan made of tinned copper. It is proposed to replace the tinned copper by the nickel-chromium steel. The remainder of the converter above the catalyst is constructed of an aluminum alloy (Al; Si, 12 to 13.5; Fe, <0.3).

The gas cooler is integral with the converter, and all parts below the catalyst are constructed of 18-8 stainless steel.

The entire absorption tower and its fittings are made of aluminum. But 18-8 stainless would have been preferred had it been available. Aluminum was found to be an ideal material from the point of view of the process materials, but trouble was being experienced by pitting on the water side by the Leverkusen cooling water.

The final scrubber is made entirely of aluminum, apart from the ceramic bubble caps. The formaldehyde cooler is aluminum, but corrosion has been experienced on the water side.

Process at McCarthy Chemical.—Gas first passes through conventional scrubbers and is then discharged through a tubular heater in order to reach the temperature required for the reaction with oxygen in the reactor. (Hightower, *loc. cit.*)

Oxidation products leaving the reaction flow to an absorption tower utilizing water as the absorbent. The solution is stripped of the chemical products in an ordinary still, and the product vapors leave the still and are condensed and fractionated.

The fractionating system for separation of the formaldehyde, acetaldehyde, and methanol consists of the customary low-pressure bubble-cap towers. Stainless steel is used in those portions of the fractionating system which are in contact with formaldehyde. A residue consisting of a water solution of salts of organic acids is withdrawn from the base of the fractionator, where methanol and water vapors are being removed prior to their final separation.

Although some of the formaldehyde is produced directly from the oxidation process, the greater part is made by oxidation of a portion of the methanol.

The methanol oxidation step involves the usual equipment and catalyst employed in this process. The methanol is vaporized in a steam heater combined with compressed air and passed through a converter containing metallic copper as the catalyst. The resulting mixture of unreacted methanol, formaldehyde, water, and residual gases is cooled and passed into a primary separation tower, where the gases are released. The mixture of formaldehyde, water, and methanol is pumped to a second tower, where formaldehyde is withdrawn from the base and sent to storage. Pumps and pipe lines carrying formaldehyde are of stainless steel.

Process of I.G. Farben.—Methanol is dehydrogenated to formaldehyde in presence of water vapor. The reaction is carried out at atmospheric pressure at 625 to 675°C. in a bed of silver granules. The reaction products are cooled and scrubbed with water, and a 30 per cent solution of formaldehyde is made.

Methanol and steam condensate are mixed and filtered through a bed of asbestos fibers and then fed to the evaporator. The methanol-steam-air mixture leaving the evaporator passes to the converter via a copper or stainless (Cr, 17; Mo, 1.8) steel and in either case is tinned internally. The mixture is raised to reaction temperature. The gas cooler lowers the reaction products to 220 to 250°C. The products are partly condensed by direct contact with condensate in the absorption tower, and the remaining cooling and condensations take place in the condensers proper. The gas leaving the condensers is scrubbed for recovery of formaldehyde and water.

Handling

Stainless Steel.—Stainless steels are often used for pumps and other equipment handling formaldehyde.

Aluminum.—This metal is used for production and handling formaldehyde but is not free from attack, which rapidly takes the form of deep pitting in ordinary commercial grades. Only the purest obtainable should be used for formaldehyde vessels, and thick material has a life far longer in proportion than thin plate and is therefore ultimately much more economical. Aluminum, however, is not so good for pipe lines or where erosion can accelerate the corrosion. (Homer, *loc. cit.*)

A New Jersey chemical plant found that a 37 per cent solution could be stored in aluminum for years. However, it seemed to penetrate the aluminum for a certain depth and then stop. Aluminum is often used for storage, piping, and other equipment.

Copper.—If the solution of formaldehyde is in contact with copper, deep discolorations ranging from blue to black may result. However, this does not impair solution strength or render it unsuitable for many uses. Tinned copper is an improvement over plain copper for service with formaldehyde. Copper stills, storage tanks, pumps, and reaction vessels are in use.

Iron and Steel.—These materials are sometimes used where discoloration is not objectionable. Corrosion may be expected but is slow enough to make plain iron and steel most economical.

Wood.—This material shrinks on exposure to formaldehyde and for this reason is not entirely suitable for bulk storage, although properly constructed barrels are used. Solutions in contact with wood may extract a small amount of resinous material and thus become discolored. (*Ibid.*)

Wooden vats have been employed, but owing to the strong shrinking action of formaldehyde on the wood, leakages are a regular occurrence for months after installation. It is generally necessary to endure this for a year or so and then reconstruct the vessel after all shrinkage has taken place; it will then give good service. (*Ibid.*)

Concrete.—Probably the most satisfactory material for bulk storage vessels is reinforced concrete. The tank is fabricated in the same manner as those for water storage and afterward lined with asphalt and acid-resistant bricks to protect the cement from attack by the formaldehyde or formic acid. A cheaper but less satisfactory lining is produced by treating the concrete, after thoroughly drying out, with paraffin wax, which is afterward melted into the surface by the careful application of a blow lamp.

Glass-lined Steel.—Among the choice of vessels for storage are glass-lined steel, rubber-lined steel, stainless steel, glass, stoneware, rubber, and aluminum.

Silver.—The use of silver in industry for handling formaldehyde is an indication of its high resistance to the attack of this chemical. Silver-lined containers have replaced other containers in many instances. (Addicks, L., "Silver in Industry," p. 374, Reinhold Publishing Corporation, New York, 1940.)

Mild Steel.—Storage tanks of mild steel can be used if a resin is applied.

Nickel, Monel, and Inconel are resistant to formaldehyde. Nickel-clad steel is used for formaldehyde storage tanks and heating coils, and Monel for agitators. Nickel pumps are used to handle formaldehyde in phenol-formaldehyde resin plants. Monel is used for cadaver tanks handling formaldehyde.

Packaging

Tank cars are lined with GR-S synthetic rubber, natural rubber, phenolic resins or vinyl resins, or stainless steel. Aluminum tank cars and drums are used also. Glass carboys are used.

FORMIC ACID

This acid is used in making its salts and esters (formates), for the coagulation of rubber latex, and for other technical operations.

Production

Process.—It can be made by the regulated oxidation of methanol and formaldehyde but is manufactured by heating sodium hydroxide with carbon monoxide at a pressure of 6 to 10 atm. (Desha, L. J., "Organic Chemistry," 1st ed., p. 237, McGraw-Hill Book Company, Inc., New York, 1936.) Formic acid is liberated by treating the sodium formate with somewhat dilute sulphuric acid. It is distilled off at reduced pressure and is concentrated by fractionation.

Glass pipe lines and storage tanks are in use. This material of construction is not only resistant to attack by formic acid and many other chemicals but supplies visibility, at times an important factor.

Handling

Stainless-steel pumps, storage tanks, and other equipment are in use. One engineer has found that stainless steel seems to be the best material for use in formic acid storage tanks. This is more expensive than plastic or rubber-lined steel, but he believes the cost is justified. Also, he installed stainless-steel condensers several years ago, and they are still in operation. They had replaced copper condenser coils which had to be installed once a year.

Natural and synthetic rubber are in use handling formic acid. The latter is reported to be more satisfactory than natural rubber.

Some companies have found copper satisfactory, especially for the final treatment of the acid. Silver-coated copper, too, is reported as useful for the final treatment. (LaQue, F. L., *Can. Chem. Process Ind.*, p. 186, May, 1938.)

Silver is said to be used in both production and handling of formic acid. It has excellent resistance to attack by formic. (Anon., Silver and Alloys, *Chem. & Met. Eng.*, Vol. 43, No. 10, p. 529, 1936.) It has been used in many applications with formic in the dyestuff industry. (Tupholme, C. H. S., Silver for Dyestuff Plant, *Am. Dyestuff Reptr.*, Vol. 25, p. 628.)

Glass pipe lines and storage tanks are in use. Durimet 20 is resistant under all conditions and is recommended at the higher concentrations and temperatures. Karbate can be used to handle all concentrations up to boiling. Both phenolic and vinyl copolymer protective coatings are resistant to the acid. Illium in boiling acid shows not more than 0.004-in. penetration per year, and in acid at 70°F. is just as resistant.

FRUIT JUICES

Processing of fruits presents a special problem because the acids contained in fruits are exceedingly corrosive to most metals. Furthermore, there is corrosion from the preservatives used for fruit juices. The principal preservative is sulphur dioxide, which is added either as the gas or more frequently as potassium metabisulphite. While sulphur dioxide is used in foreign countries as a preservative for fruit juices and possibly also for fruits, it never is used in canned products in the United States, where most of the juices are packed in cans; neither is any other preservative used in these juices.

Production

Materials of Construction.—Many metals and nonmetals are in use.

Stainless Steel.—Fruit processors have found that stainless steel is completely resistant to corrosion from acids contained in fruit, and the metal, in turn, does not impair in any way the original flavor, color, or vitamin content of the fruit.

Some of the stainless-steel equipment used in fruit-juice extraction and canning includes sorting and preparation tables, mixing tanks, extractors, and can fillers. Stainless steel is also used for concentrators, conveyors, cookers, dippers, fruit knives, heaters, parts, sinks, vacuum pans, vats, and tubing and pipe lines.

While 18-8 stainless steels are resistant to pure fruit juices, it is necessary to use the molybdenum-bearing 18-8 stainless steels when the juices contain sulphur dioxide preservative. (McWilliam, J. A., Use of Stainless Steel in Chemical and Food Process Industries, *Murex Rev.*, Vol. 1, No. 1, p. 1, 1948.)

All equipment used in the juice plant of Texsun Citrus Exchange at Weslaco, Tex., is stainless steel or aluminum, since vitamin C is catalytically oxidized by the presence of traces of iron or copper. (Shearon, W. H., and E. M. Burdick, *Ind. Eng. Chem.*, Vol. 40, No. 3, p. 370, 1948.)

Aluminum.—The action of acid fruit juices and other organic acids on aluminum is less predictable than is that of pure acids present in these products. It is an interesting fact that the total acidity or pH of a fruit juice is no criterion of its behavior toward aluminum. The addition of sugar to fruit juices reduces the attack on aluminum to a minimum. It also has been observed that, if fruit juices contact no other metals prior to coming into contact with aluminum, there is no risk of any serious attack of the aluminum. However, if the fruit acids pick up small amounts of heavy metal compounds prior to the time they come in contact with aluminum, they are likely to be quite corrosive. Aluminum orange and lemon squeezers are used extensively and with satisfactory results. However, it is doubtful if an aluminum storage tank would be suitable for the liquids if they were obtained from fruits squeezed in, for example, tinned equipment. (Aluminum Co. of America, "Aluminum in the Chemical Industry," p. 33, 1944.)

The interaction of fruit juices and aluminum has been investigated by the Research Laboratories of the British Aluminum Co. Ltd. (Gilroy, P. E., and F. A. Champion, Aluminum and Fruit Juices, *J. Soc. Chem. Ind.*, Vol. 67, pp. 407–410, 1948.) The corrosion by apple juice was very slight with no pitting, which was very largely due to the malic acid content, and was affected very little by the carbon dioxide used as preservative. With the other juices tested, the sulphur dioxide used as preservative can cause serious attack in natural or concentrated juices, but not in synthetic solutions.

High sulphur dioxide contents tended to cause structural attack of alloys and serious pitting of pure metal, especially in the vicinity of the water line and especially in lemon juice, which is the most corrosive of fruit juices. The effects were similar whether the sulphur dioxide was added as gas or as potassium metabisulphite (the latter being the usual trade method). The results indicate that, if the total sulphur dioxide content is limited to 350 ppm. for lemon juice and 700 ppm. for other juices, there will only be very slight corrosion with little or no pitting and no noticeable effect on the taste or smell of citrus juices. The color of black-currant juice and also to a very slight extent of apple juice was affected by the corrosion process, especially with lower purity aluminum, but was largely restored by aeration. For a given storage time and metal composition, the effect of the metal on the color of the juice will decrease in importance as the size of the container increases owing to the reduction in the area of metal per unit volume of the juice. Corrosion by citrus fruit juices was not much affected by the concentration of the juice and was only partly due to the citric acid content.

The following practical conclusions are drawn from these results and other information mentioned in the paper:

1. For natural and concentrated apple juice under carbon dioxide at pressures up to 120 psi., 99.8 per cent pure aluminum, 1¼ Mn and 2 per cent Mg alloys, and 99.5 per cent pure aluminum are suitable, the preference being in that order.

For acid-free apple treacle 99 per cent pure aluminum would probably suffice, except possibly with reference to the color of the juice.

2. For black-currant juice 99.8 per cent pure aluminum, 2 per cent Mg alloy, and 1¼ per cent Mn alloy are quite suitable; 99.5 per cent pure aluminum is satisfactory except perhaps for its effect on the color of the juice. Sulphur dioxide contents up to 700 ppm. would be permissible if required.

3. For lemon juice containing 0 to 350 ppm. of sulphur dioxide and for other citrus fruit juices containing 0 to 700 ppm. of sulphur dioxide, 99.8 per cent pure aluminum, 2 per cent Mg alloy, 1¼ per cent Mn alloy, and 99.5 per cent pure aluminum are preferred in that order, although there is little to choose between the first three metals.

Copper.—In the handling and processing of fruits copper and its alloys are widely used. Fruit juices and sirups and the saline solutions used in canning have a highly corrosive effect upon some materials; therefore copper, brass, and bronze are used in many operations. For example, in the canning of peaches and apricots many items of equipment made from copper or its alloys are used. Automatic pitters and slicers use brass and bronze castings. After lye peeling, peaches are handled by an elevator having copper flights and side walls. Parts of the blanchers coming into contact with the fruit are made of copper. Copper screens are used in the grader that sorts the various sizes of fruit before it drops into copper chutes that convey it to packing tables and cans. The sirup that is added at this point is handled in equipment having many copper or copper-alloy parts. (Cole, C. S., Copper, Brass and Bronze, *Food Ind.*, Vol. 7, No. 12, pp. 583–584, 1935.)

Many parts such as intermediate tanks, piping, and skimmers are made of copper, and fruit-pulping machines have all parts coming in contact with the fruit juice made of copper, brass, or bronze. Pumps are usually made of bronze. Brass is used for slicing wheels for fruit. (Copper Development Association, "Copper in Chemical Plant," p. 57, 1936.)

Nickel and Alloys.—Monel, nickel, and Inconel should be used with caution in sulphurous acid solutions of appreciable concentrations. Dilute solutions, such as are used in preservation of fruits, can be handled successfully. Inconel is superior to the other two metals from the standpoint of tarnishing.

Silver.—Pure silver and silver-lined steel condensers and pipe lines have been used in the preparation of fruit juices and extracts. (Lee, J. A., Silver, Gold, Tantalum, *Ind. Eng. Chem.*, Vol. 38, No. 12, p. 1412.)

Sterling silver cooling coils have been used for fruit sirups, especially where a slight contamination or discoloration would occur if copper, nickel, or some other metal were used. Sterling silver was used in preference to pure silver because of the lower strength of the pure metal. (Lee, J. A., Materials for Chemical Plants, *Trans. Chem. Eng. Cong. World Power Conf.*, London, Vol. 1, pp. 480–485.)

In a large beverage plant in New Jersey, sterling silver cooling coils are used for fruit sirups. The coils are inserted in cast-iron pipes, and the elbows are made of bronze with a heavy coating of silver electroplated on the interior surface.

Both calcium and sodium chloride brines cool the sirups circulating through the coils.

Neoprene.—In passing through the washing solutions, the grids of the fruit-washing machine must withstand the corrosive action of various solutions of soda ash, sodium silicate, hydrochloric acid, light mineral oils, and several types of wetting agents. The rate of corrosion is speeded up by heat and by thorough aeration occurring during the first washing operation.

After trying out metals without success, one engineer found that a successful machine can be made by using a grid made of rods of cold-rolled steel covered with neoprene.

The rods are mounted between blocks of maple, cut and curved to fit the covered rods, and held together by a tie rod of Monel. These tie rods extend through the wooden sides of the grid and so are entirely covered and protected in this way from corrosion.

Glass-lined Steel.—For processing acid foods such as fruit-flavoring concentrates, glass-lined steel distillation units are used. A glass-lined continuous de-aerator is in use.

Other Materials.—Glass piping is used to handle orange and lemon juice in concentrating plants. Worthite pumps and valves are in use. Waxed wooden barrels and tinned-iron cans have been used for transporting fruit juices; the former are difficult to keep clean and sterile and have a relatively short life, while the latter are not always satisfactory in resistance to corrosion. (Gilroy, P. E., and F. A. Champion, Aluminum and Fruit Juices, *J. Soc. Chem. Ind.*, Vol. 67, p. 707, 1948.)

Bronze bearings in a citrus-fruit press were replaced with a laminated phenolic bearing because of increased resistance to the fruit juices, which lubricate the bearings.

GELATIN

There are three types of gelatin: (1) edible, (2) inedible, and (3) photographic. The three are made from animal bones, calfskins, and pigskins. They all contain about one-third collagen by weight. Because of the need for great cleanliness and purity of gelatin intended for consumption and photographic purposes, special materials of construction are used in making gelatin for these purposes. On the other hand gelatin for inedible purposes does not call for particular purity and consequently can be produced in ordinary materials of construction.

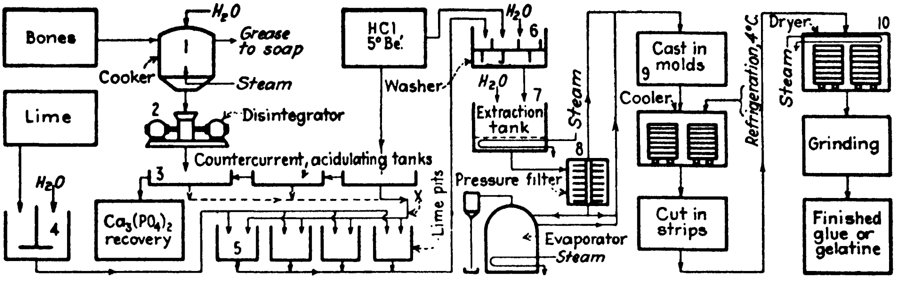
Production

Materials of Construction.—Aluminum equipment is extensively used for making edible gelatin. It is used for evaporators, storage tanks, cooking tanks, piping, dryer trays, and chutes from grinders to screens. Aluminum is one of the few metals from which equipment for the preparation of edible gelatin can be made.

Nickel, Monel, and Inconel, too, are used for edible gelatin. In one plant all equipment coming into contact with the gelatin is made of nickel or its alloys. Evaporators, drying nets, heating coils, kettles, and storage tanks are Monel or nickel. Inconel is useful for drying nets.

Edible-gelatin solutions, in course of refinement, are sometimes handled in glass-lined equipment to advantage because of their mineral acid content, thus eliminating dissolved metals as an impurity in the final product. (Barnes, P. S., Glass-lined Equipment, *Food Ind.*, Vol. 7, No. 12, pp. 590–592, 1935.)

Copper is used for concentrators, pipes, storage vessels, and mixing pans for gelatin solutions.



Note:- Manufacture of glue and gelatine differs largely in that poorer grades of raw materials and higher extracting temperatures are used for the former. Glue is more completely hydrolyzed than gelatine. Instead of bones, skins, hides, sinews, hide scraps, fleshings, fish stock, etc., may be used, in which case, after washing, they are introduced at X. Usually three extractions at temperatures from 60 to 75 deg.C. are used. The last extract requires concentration before molding

Glue and gelatin.

1. Steel
2. Steel
3. Wood
4. Steel
5. Concrete
6. Wood
7. Wood
8. Steel
9. Steel
10. Steel

Wood, too, is used in the production of gelatin. It is used for tanks in which crushed bones are treated with hydrochloric acid to separate the collagen from calcium phosphate and other mineral matter. It is also used later in the same process for extraction tanks.

Concrete vats are used in making gelatin from bones and hides. The ossein is soaked with milk of lime for several weeks.

Edible-gelatin Process.—In one edible-gelatin plant the raw materials are first soaked in nickel tanks. This soaking swells the protein, and it takes on water. This material is conveyed to the nickel cooking tanks. The gelatin goes from these tanks to nickel holding tanks. From the holding tanks it passes through a filter and is sent to the chilling room and allowed to solidify. The solid gelatin is then cut into strips and placed on Inconel wire-mesh drying frames. Then the gelatin is ground into a powder and packaged.

Inedible-gelatin Process.—When bones are used as the raw material, the procedure is slightly different, especially in the early steps in the process. They should first be degreased. This is done by heating under steam pressure and then running off the grease layer. (Shreve, R. N., "The Chemical Process Industries," 1st ed., p. 527, McGraw-Hill Book Company, Inc., New York, 1945.) The bones are then crushed and enter a battery of wooden tanks. Cold, 5°Bé. hydrochloric acid is passed countercurrent to the bones. The calcium phosphate, carbonate, and other mineral matter of the bones are dissolved, leaving the organic matter, collagen, with the residue from the bones. This is now called "ossein." It is unnecessary to treat skins with HCl because the collagen of skins is not shielded by mineral matter such as the calcium salts.

The ossein is soaked in concrete vats containing milk of lime for a month or more. This same treatment is also given to hides. When the soaking in the lime is complete, the ossein or hides are washed in a rotary drum or conical-shaped washer with water and hydrochloric acid and with water. (*Ibid.*)

The next step is extraction, which is usually performed in wooden tanks equipped with steam coils. The extraction is made with water kept at 60 to 65°C. for 8 hr. An 8 to 10 per cent solution of gelatin is obtained which is filtered hot and cooled. A second extraction is made. Filtered liquors are run into long steel trays, which are placed in refrigerated rooms to jell the contents. A third extraction of the ossein or hides is carried out at 75°C. This is darker in color and so dilute that it must be evaporated under vacuum before it is cooled.

Cooled solid gelatin is removed from the mold and cut into slabs. These slabs are spread on nets which are stacked on small mobile trucks and pushed into a drying tunnel through which filtered air at 40°C. is pulled by exhauster fans. On drying, slabs shrink to a thin strip which can be ground to a powder for further usage.

GLUTAMIC ACID

Glutamic acid is being produced from Steffens waste water from beet-sugar refineries and also from wheat gluten and other materials. Much of the equipment is rubber-covered to prevent corrosion from the hydrochloric acid used. However, the rubber has not proved entirely satisfactory. Chlorimet 3 pumps are being successfully applied in this service. Some replacements of rubber-lined plate-and-frame filter presses with wood have been made. Furthermore, difficulty has been encountered with rubber-lined pipe because salt crystals tend to deposit on the rubber surface to which they adhere. The hydrolysis is usually carried out with hot concentrated hydrochloric acid in glass-lined equipment.

Stainless steel of Type 316 seems to be fairly satisfactory in handling glutamic acid. It is not satisfactory in the presence of hydrochloric acid.

For a description of the process for making this acid see Monosodium Glutamate.

GLYCEROL DICHLOROHYDRIN

This chemical was made by a batch process at the I.G. Farben. Leverkusen plant. The reaction vessel consisted of a glazed earthenware pot immersed in a steam-heated oil bath. The pot carried two inlet and one outlet pipes of glass and a thermometer. Hydrochloric acid gas was generated by dropping 96 per cent sulphuric acid into concentrated hydrochloric acid, the quantities being such that the resultant sulphuric acid was of 80 per cent strength. Two generators were used.

Glycerol was charged to the pot, heated to 80 to 100°C., and the hydrochloric acid passed in via a sulphuric acid wash bottle during about 20 hr. The temperature rose to about 110°C. The vapors emerging passed through a glass Liebig condenser to a chemical-stoneware receiver before passing to the absorption system. The condensate was neutralized to faint acidity with chalk, and the oily layer added to the main production.

The crude dichlorohydrin was drawn into a pot and distilled in vacuum through a ring-packed glass column to an earthenware receiver. (Adams, D. A. W., and W. Baird, Some Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.)

GLYCEROL MONOCHLOROHYDRIN

The manufacture was carried out by a continuous process at the German I.G. Farben.'s Leverkusen plant. (Adams, D. A. W., and W. Baird, Some Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.)

Production

Process.—The unit consists of a column made up of five separate segments of quartz pipe 100 cm. long by 20 cm. i.d., each segment being connected individually to five similar quartz tubes contained together in a gas-heated glycerol bath. The circuit is such that glycerol fed to the top of the highest segment flows through this column, runs from the bottom to the bottom of the tube in the oil bath and from the top of this to the top of the next segment in the column and so on. Hydrochloric acid is fed to the bottom of the lowest segment in the column, and the liquid outlet is also here.

The glycerin containing 1½ per cent acetic acid as catalyst is preheated to 80°C. and fed in at a rate of 10 to 11 kg. per hr. The temperature in the oil bath is maintained at 110°, the temperature difference inducing liquid flow through the system. The reason for what seems a complicated procedure is that glycerol forms an additive complex with hydrochloric acid which is only partly converted to chlorohydrin on heating at 110° and the remainder dissociated into its components: a cycle of treatments is, therefore, necessary to give a satisfactory yield.

The hydrochloric acid gas is obtained as by-product from salt-cake ovens and should contain at least 50 per cent HCl by volume. The acid passes countercurrent to the glycerol at such a rate that absorption is almost complete, only a little passing to the chimney; the passage of the gases is facilitated by a slight suction at the exit end.

The crude chlorohydrin can be distilled batchwise, but a Jena glass unit has been constructed for continuous distillation. The first distillation is essentially a topping process and gives crude chlorohydrin of about 90 per cent purity which can be redistilled continuously in a similar apparatus to give 98 per cent pure material.

GRAPE JUICE

As is the case in the wine industry it is essential to use materials of construction that will not affect the color or flavor of the juice.

Production

Materials of Construction.—18-8 stainless steel or glass-lined steel is used for many of the important pieces of equipment, since they are immune to the foods and acids encountered in handling and processing of grape juice.

Process.—A modern grape-juice plant is exemplified by the Naples, N.Y., plant of Widmer's Wine Cellars, Inc. (Anon., Widmer's New Production Line in Action, *Glass Lining*, Vol. 14, No. 3, p. 5, 1943.) In this plant incoming grapes are dumped into a washer-conveyor, which takes them to a stemming machine. Stems go out one chute, grapes go into a stainless-steel steam-jacketed cooking kettle. These are equipped with stainless-steel agitators. Here the product in the kettles is raised to 140°F. The hot grapes go to a hydraulic press. Frames containing the trays of grapes are mounted on trucks running in front of and behind each press. In front of each press truck station is a stainless-steel funnel. Funnels are connected by pipe to receiving kettles under the presses. There are two stainless and one glass-lined kettle. Juice is pumped to stainless-steel jacketed kettles. These act as balance tanks and also maintain the temperature of pressed juice at 120°F. prior to actual pasteurization. From these kettles, the juice flows by gravity through a continuous pasteurizer which supplies the filling machines. Some juice is only flash pasteurized and then cooled and pumped through aluminum pipe line to a refrigerating plant.

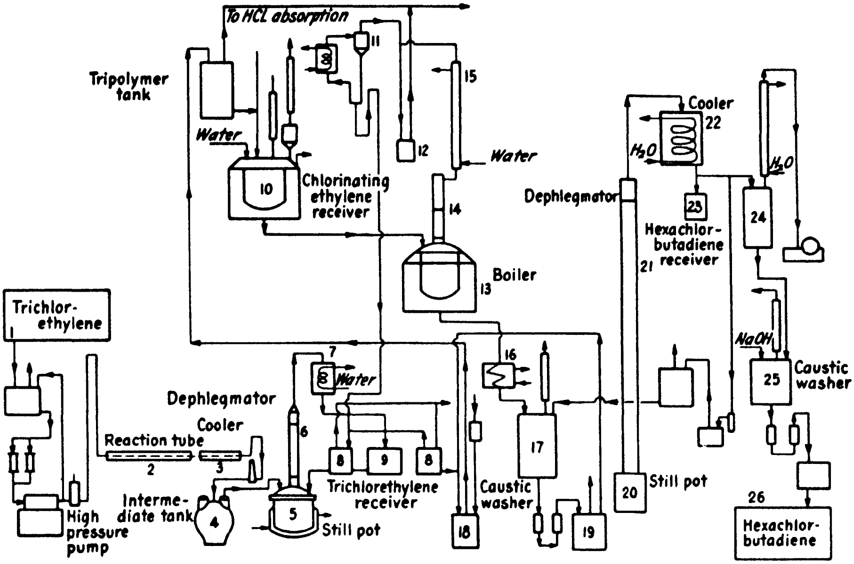
GUANIDINE NITRATE

Guanidine nitrate is prepared by dissolving 10.8 parts by weight of recrystallized dicyandiamide and 20.4 parts of ammonium nitrate in 19.2 parts of liquid ammonia (U.S. Patent 2,252,400). The mixture is charged into an autoclave fabricated from 18-8 stabilized stainless steel and equipped with internal heating coils and an agitator. (Groggins, P. H., "Unit Processes in Organic Synthesis," 3d ed., p. 414, McGraw-Hill Book Company, Inc., New York, 1947.)

The autoclave is heated by pumping a liquid mixture of diphenyl and diphenyl oxide, Dowtherm, at 180°C. through the coils, and a reaction temperature of 180°C. is maintained for ½ hr. The autoclave is then cooled and discharged, and the ammonia is evaporated. The resultant product comprises 29.9 parts of crude quanidine nitrate.

HEXACHLORBUTADIENE

Hexachlorbutadiene was made from trichlorethylene in a semicommercial plant at Burghausen, Germany, by Alexander Wacker A.G. (Carpenter, G. B., Chlorinated Hydrocarbons from Acetylene, FIAT Final Report 843, Technical Industrial Intelligence Division, U.S. Department of Commerce.)



Hexachlorbutadiene.

1. Lead-lined steel
2. Glass-lined steel
3. Copper
4. Stoneware
5. Homogeneous lead-lined steel
6. Homogeneous lead-lined steel
7. Lead
8. Homogeneous lead-lined steel
9. Homogeneous lead-lined steel
10. Homogeneous lead-lined steel
11. Homogeneous lead-lined steel
12. Glass
13. Steel
14. Steel
15. Steel
16. Steel
17. Steel
18. Homogeneous lead-lined steel

19–26. Steel

Production

Materials of Construction.—Considerable corrosion occurs unless special materials of construction are used. The reaction tube is glass-lined steel. A silver-lined tube was tested, but corrosion difficulties were encountered. The hexachlorbutene is distilled in a lead-lined column. It is treated with ferric chloride in a lead-lined tank. Stoneware is used for an intermediate tank. One

Liebig cooler is copper; another is steel with lead pipe. Much of the other equipment is lead-lined steel.

Process.—Trichlorethylene is continuously polymerized by heat and pressure. It is conveyed by a bronze pump to a glass-lined steel tube 50 mm. i.d. Three external electric furnaces heat the tube. The reaction temperature is 220°C. Conversion to hexachlorbutene is 30 per cent per pass. The product is cooled to 20°C. and charged to a homogeneously lead-lined batch still, where it is fractionated. The unreacted trichlorethylene is distilled at atmospheric pressure, and the hexachlorbutene at 15 to 30 mm. Hg abs. pressure. A lead-lined column packed with raschig rings is used.

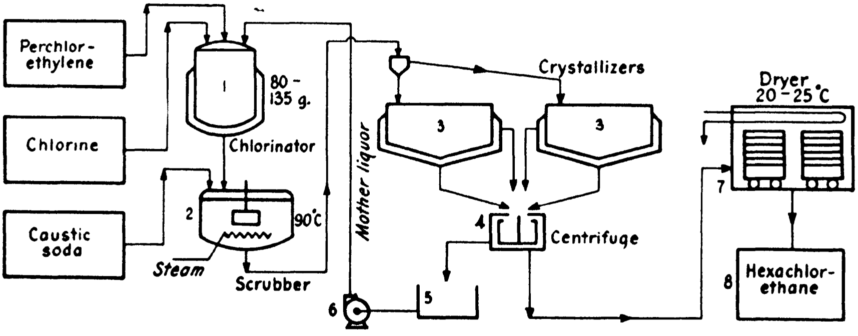
Hexachlorbutene, together with ferric chloride, is charged to a lead-lined steam-jacketed tank. It is first heated to 180°C. to split off 1 mole of hydrogen chloride and then reacted with chlorine at 75°C. to form heptachlorbutene.

The crude product is transferred to a lead-lined tank and heated at 205°C. for 8 hr. One mole of hydrogen chloride is split off, and the product is hexachlorbutadiene. The crude product is charged into a batch still. The fractionating column is packed with raschig rings. A dephlegmator supplies the reflux. The product is washed with 10 per cent caustic soda for 4 hr. at 90°C. and is ready for sale.

The hydrogen chloride evolved in two steps of the reaction is absorbed with water in a glass tower.

HEXACHLORETHANE

This chemical is made from perchlorethylene by batch chlorination in lead-lined jacketed kettles in the Burghausen plant of Alexander Wacker A.G. (Carpenter, G. B., Chlorinated Hydrocarbons from Acetylene, FIAT Final Report 843, Technical Industrial Intelligence Division, U.S. Department of Commerce.)



Hexachlorethane.

1. Lead-lined
2. Concrete
3. Lead-lined
4. Copper-lined
5. Iron
6. Iron
7. Wood
8. Wood

Production

Materials of Construction.—Lead-lined equipment is used for the chlorination vessel and the crystallizing basins. The scrubber is concrete, the centrifuge copper-lined, the mother-liquor tank and pump iron, and the dryer wood. In the United States, nickel-clad steel is used for rotary vacuum dryers and nozzles.

Process.—A charge of pure perchlorethylene containing ferric chloride, together with mother liquor containing 10 per cent hexachlorethane, is put in the lead-lined jacketed reactor and heated to 80°C. Over a period of 18 hr. about 600 kg. of chlorine is added while the temperature is raised to 136°C. The product contains 60 per cent hexachlorethane and is discharged into a concrete tank containing a stirrer. Caustic solution is added, and the mixture stirred for 4 hr. The temperature is held at 90°C. by injection of steam. The water layer is run to the sewer and carries off the precipitated ferric hydroxide.

The washed crude product is then dumped into lead-lined crystallizing tanks. The tanks have cooling water jackets, and crystallization is complete in 24 hr. Crystals are separated in a copper-lined centrifuge. The mother liquor containing about 10 per cent hexachlorethane is recycled to the chlorinators. The crystalline hexachlorethane contains 10 per cent perchlorethylene and is spread on wooden shelves in a drying room. The room temperature is maintained at 20 to 25°C.

Packaging

Dried hexachlorethane crystals are packed in wooden barrels for shipment.

HEXAFLUOROXYLENE

Coal-tar xylene is charged into a chlorinator and chlorine introduced in the production of hexafluoroxylene. Chlorination is continued until a specific gravity of 1.6 at 25°C. is reached. The hexachloroxylene is charged into a steel autoclave. Liquid hydrogen fluoride is added to the chloroxylene through a pump under slight pressure, since vent valves attached to the autoclave are closed to minimize hydrogen fluoride losses. Heat is applied through coils. After the reaction is complete, the temperature is reduced. By venting through a steel blowdown tank the pressure is dropped. The autoclave is then discharged into the blowdown tank.

To ensure removal of the acids from the fluorinated material prior to subsequent processing, the latter is neutralized with caustic and filtered. This material is subjected to steam distillation from an iron still. Benzotrifluoride, hexafluoroxylene, and the chlorofluoroxylenes are separated from a residue. Water is separated.

Distillation in an iron still serves as a means of isolating the desired material from most of the chlorofluoroxylenes and unstable intermediates. The hexafluoroxylene fraction is further rectified by distillation through a column, and the product collected. (Murray, R. L., *et al.*, Production of Bis (Trifluoromethyl) Benzene, *Ind. Eng. Chem.*, Vol. 39, No. 3, p. 302, 1947.)

HEXAMETHYLENE DIAMMONIUM ADIPATE

Production

Materials of Construction.—Few of the materials used in making this chemical are by their nature corrosive. The materials of construction problem was not one of prevention of corrosion but one of maintaining purity and clarity of the product. Hence all equipment which touches the product in any way is made of stainless steel, most of it Type 347. Inconel is used for ammonia superheaters.

Process.—Nylon salt, hexamethylene diammonium adipate, is made in the Washington, W.Va., Works of Du Pont with a dibasic acid and a diamine. The acids are primarily adipic and sebacic acids. The primary diamine is hexamethylene diamine. The acid, which is solid, is dissolved in water in a stainless-steel, agitated vessel called a "salt kettle." This vessel is water-jacketed to remove the heat of reaction. Then the diamine is slowly added, at such a rate that temperature rise can be controlled, until the proper quantity to react with the acid has been put in. Control is by pH of the liquid contents.

The product of the reaction is a dilute solution of hexamethylene diammonium adipate in water. The dilution is just enough to prevent crystallization at atmospheric temperatures. To give the future polymer better color and guard against impurities, this solution is next slurried with activated carbon and filtered through a Niagara-type pressure filter.

Next step is concentration of the salt solution. This is done in a stainless-steel Conkey-type evaporator, heated with steam. (Williams, R., Jr., How Washington Works, *Chem. Eng.*, Vol. 55, No. 9, pp. 118–121, 1948.)

HEXAMETHYLENE DIAMMONIUM ADIPATE POLYMER (NYLON)

Hexamethylene diammonium adipate salt is polymerized and made into plastic molding powder, monofilaments, and yarn. These operations are carried out in several plants of E. I. du Pont de Nemours & Co.

Production

Materials of Construction.—Few of the materials used at these plants are by their nature corrosive. The materials of construction problem was not one of prevention of corrosion but one of maintaining purity and clarity of the product. Hence all equipment which touches the product in any way is made of stainless steel, most of it Type 347.

Process.—The process can be considered as starting with the nylon salt, hexamethylene diammonium adipate. The dilute solution is first concentrated in a stainless-steel, Conkey-type evaporator. Operation is batchwise. The highly concentrated salt solution then feeds by gravity to autoclaves.

In the autoclaves final removal of solution water and polymerization occur. These units are stainless-steel kettles which are jacketed and have internal cooling coils. They are heated with Dowtherm. When the polymer has reached the desired molecular weight, the reaction is stopped by cooling down to just above the melting point.

To get the polymer out of the autoclave inert gas pressure is applied within the vessel. Molten nylon has quite low viscosity and is easy to get to flow from the kettle.

The extrusion valve is slotted so that the nylon comes out of the autoclave in the form of a ribbon. This ribbon drops onto a chilled wheel called a casting wheel to a thin flexible ribbon. The ribbon is then dried and passed through a cube cutter, thus producing the final molding-powder product, when no colors or additive are required.

Monofilament.—Conversion of nylon polymer into level end tapered monofilaments is done at the Washington, W.Va., works of the Du Pont company. (Williams, Roger, Jr., How Washington Works, *Chem. Eng.*, Vol. 55, No. 9, pp. 118–121, 1948.)

The first step is the extrusion machine. The solid nylon is melted under pressure, using Dowtherm vapor. Then it extrudes several filaments at a time, through a nozzle. Because there is tension on the threads, the nylon is in essence "pulled" out of the nozzle. As it leaves the nozzle it is immediately passed through a water quench bath and then between a pair of pinch rolls.

It is these pinch rolls that produce the taper. The rolls are alternately speeded up and slowed down so that the nylon coming from the nozzle first comes out faster, and hence thinner; and then more slowly, and hence thicker.

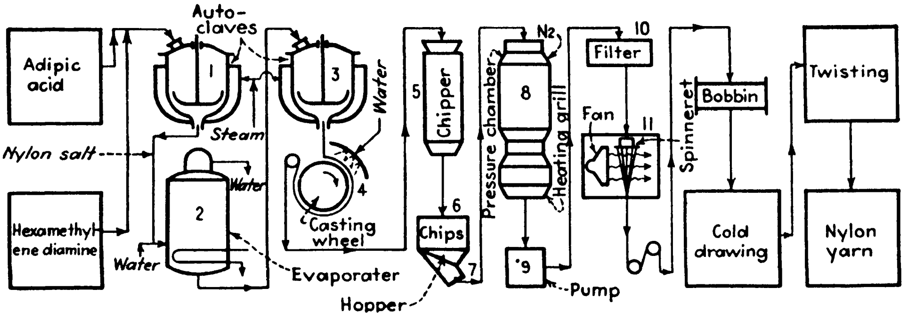
Next the nylon has to be drawn to orient the polymer molecules and gain greater strength. Drawing an uneven filament without breaking the thin sections, and yet still getting sufficient drawing of the thick sections, is a trick in itself. Then the continuous filament goes through a conditioning chamber and is continuously rolled up on spools. The spooling equipment is so arranged that switching from one spool to another can be accomplished without interruption of the process, and without loss of material.

Now the problem is the cutting of the continuous filament into short lengths of tapered bristle. The spool is unwound through a mechanical "feeler" that measures the thickness, activates a solenoid which then causes a cutter to come down and cut the thick-thin thread at exactly the thick position. These cuts, with thick ends and a thin center, continue down a conveyor and are automatically brushed off at right angles onto another conveyor belt. In this direction an operator can pick them up in bunches, and by holding the ends of each bunch put them into a machine which cuts the bunch in the middle. Hence small bunches of bristles are obtained which are tapered with the thin ends all at one end of the bunch. These are then trimmed and packaged.

Yarn.—The polymer is converted into yarn at several Du Pont plants. The technique used in the Seaford, Del., plant is described. (Lee, J. A., Nylon Production Technique Is Unique, *Chem. & Met. Eng.*, Vol. 43, No. 3, pp. 96–99, 1946.)

Chips and flakes of nylon polymer are stored in storage blenders. The bottoms of the blenders extend through to the floor below, where chutes from them empty into transfer hoppers operating on a monorail. The polymer is conveyed to individual supply hoppers which feed the spinning unit.

When the supply hopper has been freed of oxygen and loaded with polymer, the plug cock is opened permitting the flake to fall by gravity into the spinning unit which is composed of a metal block surrounded by a Dowtherm vapor-heated jacket. This keeps the temperature of the metal block above the melting point of the material. In this block there is a Dowtherm vapor-heated grid. When the flake comes in contact with the grid, it melts and dribbles through to a melt chamber, which is a small reservoir below.



Nylon yarn. All stainless steel except 7, which is aluminum.

From this chamber there are portholes which lead to the gear spinning pumps. The pumps deliver the polymer to a sand filter, which is followed by a screen and the spinneret. Throughout these operations air must be excluded to avoid oxidation.

Filaments pass down through a cooling chimney. They next pass through a converging guide which gathers them into a bundle. The bundle continues on its journey, passing through a chamber in which the yarn is humidified by steam in order to bring its moisture content up to equilibrium. The moistened yarn passes over a glass finish roll which applies an oil emulsion. This serves as a lubricant in subsequent operations and also to bind the filaments together so that the windup package will be more stable toward deformation.

The yarn is stretched or drawn to the desired degree by running it through a system of rollers in such a manner that it is extended to four or more times its original length, depending upon the particular polyamide being processed. A highly interesting phenomenon occurs during the stretching operation. The long, chainlike molecules which make up the undrawn fiber are arranged in a helter-skelter fashion but on drawing orient themselves. It is this operation which develops the strength and elasticity characteristic of nylon.

HEXAMETHYLENE DIISOCYANATE

Hexamethylene diamine was a very important starting material for the polyurethane type of synthetic polymers. The diisocyanates were produced at the Leverkusen (Germany) plant and made into polymers at the Wolfen Film Fabrik and at Ludwigshafen. (Boundy, R. H., and R. L. Hasche, Manufacturing of Thermoplastics in Plants of I.G. Farben., Report 1069, Combined Intelligence Objectives Committee, U.S. Department of Commerce.)

Production

Process.—The diisocyanate was prepared from hexamethylene diamine and phosgene using *o*-dichlorobenzene as a solvent. The reaction was carried out in a stainless-steel autoclave. One mole of phosgene was introduced slowly, maintaining the temperature at 0 to 5°C. The second mole of phosgene was then added, allowing the temperature to rise to 140 to 180°C.

The autoclave was then heated, the phosgene boiled off at atmospheric pressure, and the *o*-dichlorobenzene removed under vacuum, employing a small amount of nitrogen. The product was then distilled in glass-lined equipment to remove the pure diisocyanate with a boiling point of 118°C.

HEXAMETHYLENETETRAMINE

The plant and equipment to be described were part of an R.D.X. plant built in Great Britain. The hexamine section was divided into four parts: (1) formaldehyde production, (2) ammonia production, (3) hexamine production, and (4) methanol recovery and distillation. (Simmons *et al.*, Manufacture of R.D.X. in Great Britain, *Ind. Chemist*, Vol. 24, No. 283, pp. 530–544, 1948.)

Production

Materials of Construction.—Aluminum was used for the reaction vessels. Coolers and centrifuges were stainless steel. Receivers were glass-lined.

Process.—The hexamine plant proper was built to suit very stringent requirements. The whole product had to pass a specification of quite abnormal severity and, in addition to the more usual requirements of chemical purity and grist size, it was essential that the material be free flowing.

The plant consists of four main sections: reaction, evaporation, centrifuging, and drying. There are two reaction vessels of welded aluminum construction, 8 ft. 6 in. in diameter and 12 ft. high. In the base of each is a circular perforated aluminum pipe to act as an ammonia distributor. Each vessel has its own circulating pump and cooler and is vented to atmosphere. The heat of reaction is considerable, and as some decomposition of hexamine takes place above 60°C., the reacting liquor is circulated through coolers (stainless-steel calandria type) by stainless-steel centrifugal pumps. The reaction is complete when slight excess of ammonia is present, the entire cycle taking about 3 hr.

The charge for the vessel is 8 short tons of formalin solution, 1.2 tons of ammonia gas, and 5.5 to 6 tons of centrifugal drain liquor. This gives a total weight of hexamine per batch of 4.9 tons, about 3 of which is new hexamine. The liquor from the reaction vessel runs to a mild-steel glass-lined cylindrical receiver whence it is fed to a salting-type vacuum evaporator built entirely of stainless steel. The vapors from the evaporator containing 10 to 12 per cent of methanol are condensed in surface condensers and pass to the methanol recovery plant. The crystals of hexamide made in the evaporator flow by gravity through a stirred salt box to overdriven centrifugals, with baskets and casings of stainless steel and shafts of mild steel sheathed with stainless.

The salt coming from the centrifugals contains about 1 per cent water and is dried in a vibrating tray dryer, consisting of an enclosed shaker conveyor mounted on hickory springs and vibrated by a shaft motor actuated through a multispeed gear with a V-rope drive. The gear enables the time of passage of salt through the dryer to be controlled. The conveyor consists of an enclosed metal box with a double bottom, the upper bottom being stepped to form a number of trays with air slits between. Steam-heated air is blown onto the bottom of the trays, and the step plates are curved in such a way that no salt falls through the slits. The dried hexamine passes to conveyor system and is packed for export or prepared for immediate nitration. Some 6 in. above the dryer trays a row of dust screens is fixed, and through these all the air from the dryer has to pass.

HEXYLALCOHOLS

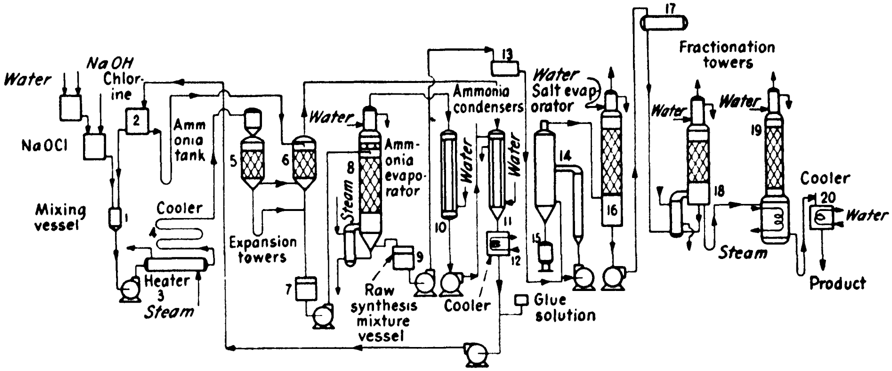
Both *n*- and isohexylalcohols were produced by treating a mixture of acetaldehyde and butyraldehyde with dilute sodium hydroxide under carefully controlled conditions and subsequently hydrogenizing the distilled unsaturated aldehydes in the presence of a copper catalyst, followed by separation of the hexylalcohols under vacuum.

Process.—Into the iron aldol boiler a mixture of acetaldehyde and butyraldehyde flows continuously in the proportion of 5:1. At the same time, 5 per cent of a solution of 2*N* NaOH is added based on the mixed aldehydes. The temperature is kept between 6 and 14°F. and circulated with a pump for 5 hr., after which the mixture runs out of the afterreaction system with an addition of excess acetic acid amounting to 20 g. per l. The acid mixture flows into a storage tank and is then drawn as required for discontinuous distillation under normal pressure in copper stills, 10 per cent of water is added, and the acetaldehyde is fractionated. Subsequently, the remaining unsaturated C_4, C_6, C_8 aldehydes are separated by steam distillation, and the condensed water returned. When the operation is completed, the waste water is drained off. The unsaturated C_4, C_6, C_8 aldehydes are then hydrogenated by circulation with excess hydrogen at a temperature between 190 and 210°F. in the presence of a reduced copper catalyst laid on pumice. Out of the circulation gas the alcohols are condensed and separated, with 20 per cent of the higher alcohols remaining as residue. The higher alcohols are then separated under vacuum of 20 to 30 mm. Hg. The ratio of *n*-hexyl- to isohexylalcohol is about 1½:5 and that of the C_6 to C_8 alcohols about 9:1.

The hexylalcohols are used for the preparation of acids, pharmaceuticals, and plasticizers.

HYDRAZINE HYDRATE

A group of American engineers investigated the hydrazine hydrate plant at Gersthofen, Germany, operated by the Chemische Fabrik, von Trausche & Co.



Hydrazine hydrate.

1. Glass
2. Steel
3. Steel
4. Steel
5. Steel with porcelain rings
6. Steel with porcelain rings
7. Steel
8. Steel with porcelain rings
9. Steel
10. Steel
11. Steel
12. Steel
13. Steel
14. 19 Cr, 9 Ni, 2 Mo stainless steel
15. 18-8 stainless steel
16. 18-8 stainless steel shell and packing
17. 18-8 stainless steel
18. 18-8 stainless steel shell and packing
19. 18-8 stainless steel shell and packing
20. 18-8 stainless steel

It was by far the largest production source of the hydrate in that country. The process in use was based on the raschig reaction of partial oxidation of ammonia by sodium hypochlorite. (Robell, J., Production of Hydrazine Hydrate Base Rocket Fuel, FIAT Final Report 839, Technical Industrial Intelligence Branch, U.S. Department of Commerce, 1948.)

Production

Materials of Construction.—For making the sodium hypochlorite there are steel tanks for diluting the caustic and iron pumps for handling the caustic. The reactors are steel lined with polyvinyl chloride. They have ceramic water-cooled coils. The vessels are covered with wooden lids. Coolers following the reactors are almost identical with the reaction vessels, the only difference being that the water flows outside the coils. The piping for sodium hypochlorite is made of polyvinyl chloride. The pumps are porcelain.

In the hydrazine hydrate part of the plant the high-pressure pump is made of cast steel, its plungers are chromium-plated, and the cylinders have steel liners. The stuffing box is packed with regular high-pressure-steam graphitized-asbestos packing. The salt evaporator is Type 316 stainless steel. All piping and equipment before the salt evaporator are made of plain steel, while that after the evaporator are 18-8 stainless steel unless otherwise mentioned.

Steel storage tanks are provided for ammonia. Oppanol-lined steel tanks are used for storing hydrazine hydrate. They are provided with 18-8 stainless-steel pumps. Steel storage tanks handle methanol.

Process.—A stream of 28.3 per cent aqua ammonia and 1*N* sodium hypochloride solution flows into a glass mixing vessel where the two streams come in close contact with each other. A single-stage, high-pressure pump takes suction from the mixing vessel and compresses the fluid to 30 atm. into a steam heater. The raw synthesis mixture flows through the tubes with steam outside the tubes.

The mixture flows through a hairpin coil, which allows additional time for the reaction to take place. From there the liquid is expanded through a regulating valve, the pressure is reduced to atmospheric, and the fluid is conducted through two expansion towers filled with porcelain raschig rings. The reduction of pressure causes the liquid to boil, large quantities of ammonia are driven off, and the solution cools to 70 to 80°C. The gas is condensed. The remaining ammonia is driven off in an evaporator filled with porcelain raschig rings.

The solution leaving the evaporator is collected in a vessel and pumped to a constant-level tank from which it flows to a salt evaporator. Here the salt is separated.

The salt evaporator has given most trouble during the development of the process, mainly by salt obstructions in the heater section. This difficulty was overcome by using a liquid velocity over 4.5 m. per sec. in the heater tubes. These tubes have to be smooth, seamless, made from stainless steel (Cr, 19; Ni, 9; Mo, 2).

Vapor coming from the top of the salt separator contains 3 per cent of hydrazine hydrate and is conducted to three fractionating towers arranged in series. Originally porcelain rings were used. After a few weeks of operation an attack was noticed. There was a formation of hydrazine zeolite which decomposed in the heaters of the last two fractionating towers and deposited porcelain in the tubes. Following this the packing was replaced with 18-8 stainless-steel turnings, which proved entirely satisfactory.

Into the first fractionating tower the vapors are introduced from the bottom. The top is provided with a reflux condenser, and the condensate washes out the hydrazine hydrate from the ascending stream. By properly proportioning this tower it is possible to obtain a pure 15 per cent hydrazine hydrate solution coming from the bottom, which is pumped to storage from which it is introduced into the second fractionating tower. This tower is also filled with 18-8 stainless turnings and provided with a reflux condenser. With a reflux ratio of 2:1 the concentration of the hydrazine hydrate solution is brought to 50 to 55 per cent.

From this tower the 50 per cent solution is introduced into another. With a reflux ratio of 4:1, a 100 per cent concentration can be reached. The final product is cooled and pumped to storage by 18-8 stainless-steel pumps.

HYDRAZINE HYDROCHLORIDE—HYDROCHLORIC ACID

In the handling of a mixture of hydrazine hydrochloride and hydrochloric acid Saran-lined steel pipe has been found to last 20 times as long at 20 to 90°C. as does copper pipe. Experience was confined to a 2½-in. line from a reactor to a cooler. Glass-lined steel is satisfactory at relatively high temperatures.

HYDROABIETYL ALCOHOL

This is a base from which a wide variety of products may be derived. Since it is made at high pressures, special alloys are required.

Production

Materials of Construction.—The Abalyn resin (methyl ester of rosin) feed lines prior to the high-pressure Aldrich pumps are black iron. From this point through the low-pressure separator the pipe lines are stainless steel. From there on all equipment is made of aluminum to prevent discoloration or contamination of product. (Lee, J. A., Hercules Makes Resins from Rosin, *Chem. Eng.*, Vol. 55, No. 11, pp. 129–132, 1948.)

Reactors are tall forged, Type 304 stainless-steel vessels. Each one is located in a concrete barricade. The closure at the top and bottom of the reactor is interesting. The seat is on the side of the reactor. The head moves with respect to the retaining flange, which forces the copper gasket outward against the reactor walls so that greater pressure means less opportunity for leaks.

Process.—Hydroabietyl alcohol is made by the hydrogenolysis of Abalyn resin at high pressure. This resin, the principal constituent of which is methyl abietate, is made from rosin. The process and materials of construction can be found on page 211 under Methyl Abietate. To make the alcohol the Abalyn is pumped at 90°F. to feed tanks. It then goes to Aldrich pumps, which increase the pressure.

The hydrogen and Abalyn are brought together in a stainless-steel mixing block. The mixture goes to a preheater. After the temperature of the mixture is raised almost to the reaction point, the mixture passes to the Abalyn feed header, a line connecting all reactors. A second stainless-steel preheater is used for making the final adjustments in the temperature. The mixture then enters the bottom of the reactors.

When leaving the second of the reactors the products pass to a stainless-steel high-pressure separator located in a concrete barricade. Here the excess hydrogen and methanol passes the low-pressure separator maintained at 10-lb. pressure. From here the hydroabietyl alcohol goes to the aluminum cooler and then through the full-flow filter.

Packaging

The product is stored and shipped in steel drums.

HYDROCHLORIC ACID

Hydrogen chloride is a gas at ordinary temperatures and pressures. Aqueous solutions of it are known as "hydrochloric acid" or, if significant amounts of impurities are present, as "muriatic acid." The common acids of commerce are 18°Bé. (1.142 sp. gr.) or 27.9 per cent HCl, 20°Bé. (1.160 sp. gr.) or 32.0 per cent HCl, and 22°Bé. (1.179 sp. gr.) or 35.8 per cent HCl. (Shreve, R. N., "The Chemical Process Industries," p. 415, McGraw-Hill Book Company, Inc., New York, 1945.)

Production

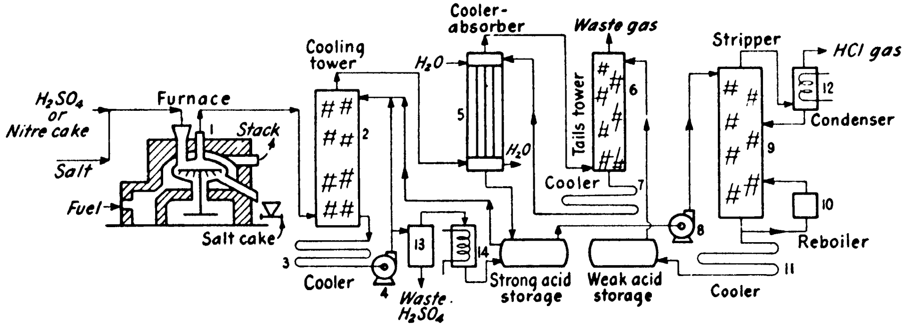
This acid is made by several processes. In the long-established process salt is treated with sulphuric acid. The by-product is salt cake. Synthetic hydrochloric acid is made in electrolytic cell plants by combining the hydrogen liberated at the cathode and chlorine at the anode of the cells. It results in a very pure acid. In addition to these methods of making acid, some acid is derived as a by-product in organic syntheses such as the production of chlorbenzene.

The question naturally arises as to why should hydrogen chloride be synthesized when it can be readily and economically made by the reaction of salt and sulphuric acid while the synthesis entails the elaborate procedure of isolating chlorine and then combining it with hydrogen. (Maude, A. H., Synthetic Hydrogen Chloride, *Chem. Eng. Progress,* Vol. 44, No. 3, p. 179, 1948.) The answer lies in a few prime considerations: (1) In using the salt-cake process, the sodium in the salt consumed yields sodium sulphate, whereas in making synthetic hydrogen chloride, the sodium results in caustic soda and according to market conditions, there may or may not be an economical outlet for one or other of these products; (2) the hydrogen chloride produced synthetically is much purer than the product from any salt-cake furnace; and (3) in some cases chlorine is available at a relatively low cost because it is in a diluted condition or because of the need for balancing the electrolytic production of caustic.

Materials of Construction (Salt Process).—In this process the materials most generally used are the nonmetallics, impervious graphite, Haveg, acid-proof brick, and rubber linings. The recovery of hydrogen chloride requires the handling, transfer, heating, and cooling of various concentrations of hydrochloric acid or hydrogen chloride gas in any concentration.

Maintenance problems with impervious graphite equipment are not difficult after a technique for handling the material has been developed. The ease with which the material can be machined (ordinary working tools are sufficient to cut nearly any shape from graphite) and the facility with which it can be cemented together make repairs and replacements fairly simple. To change a piping layout, for example, the plant maintenance crew seldom bothers to change fittings. They cut out the broken section with a hacksaw, cut a replacement piece to proper size, and cement it in place. (Armstrong, W. F., Construction Materials in Mannheim HCl Plant, *Chem. Eng.*, Vol. 54, No. 8, pp. 96–98, 1947.)

When repairs are necessary, successful use has been made of impervious graphite patches. These are simply blocks or slabs of this material cemented in place over the area involved and have been placed both inside and outside tower sections. Impervious graphite patches have been used to repair temporarily the holes that have developed in the linings of rubber-lined tanks.



Hydrochloric acid (salt process).

1. Refractory-lined steel
2. Acid-proof brick-lined steel, stoneware
3. Silica, impervious graphite
4. Impervious graphite
5. Impervious graphite
6. Haveg with porcelain rings
7. Impervious graphite
8. Impervious graphite
9. Impervious graphite
10. Steel with impervious graphite tubes
11. Impervious graphite
12. Steel with impervious graphite tubes
13. Steel with impervious graphite tubes
14. Steel with impervious graphite tubes

The phenolic resin material Haveg is used for housings and other parts of equipment because of its corrosion resistance. Gas lines in some cases are made of this synthetic resin. Necessary tanks, fans, etc., are rubber-lined. Acidproof brick is used for cooling towers and other equipment.

All steel equipment is protected by acid-resisting coatings. Pumps are sometimes made of high-silicon iron or Karbate. In some cases pumps are nonstuffing box type made of Haveg with Hastelloy B trim. Valves can be made of the same alloy.

In one plant visited by the author the building was steel with Transite siding. Such wood as was used for decking and platforms around the hydrochloric area was given a special impregnation for fire and acid resistance. Metallic equipment had been so designed that parts known to have only a short life due to high rate of corrosion could be quickly and easily replaced.

Materials of Construction (Synthetic Process).—Equipment for use in this process has been described in the literature. (Maude, *loc. cit.*) There are four main types of chlorine burners: silica burners, ceramic-lined burners, impregnated graphite burners, and the water-jacketed steel burners. The silica burner is relatively inexpensive, but it produces gas contaminated with air. It is suitable for synthesizing hydrogen chloride for the purpose of making muriatic acid, particularly on a small scale, but it is difficult to construct such units in large sizes.

A brick-lined burner can be built entirely airtight but has the disadvantage of large size and the delivery of gas which is inconveniently hot.

Burners of impregnated graphite can be made gastight and are suitable for burning wet gases. The heat of combustion is carried away by water cooling.

Water-jacketed burners of steel construction are probably the most economical units where high-grade hydrogen chloride is to be made from dried chlorine and hydrogen. The lining of the combustion chamber is held at a temperature precluding the condensation of corrosive dew. The temperature is also such as to prevent damage by heat.

Copper is not a suitable material of construction. It appears that a copper weld or even a copper sheet made of commercial deoxidized copper is liable to develop submicroscopic leaks in the course of time.

Steel turned out to be satisfactory, and burners with ¼ in. thick shell gave 4 years of service. It is probable that the corrosion occurred mainly during shutdown periods, when the equipment was cold and when moist air may have leaked into the equipment.

The gas exit pipe from the burner acts as a cooler for the hydrogen chloride. Usually the temperature of the gas must be substantially reduced before it is utilized. This can conveniently be done by lengths of pipe exposed to the atmosphere. But where the temperature of the wall of the pipe is lower than the dew point, a corrosive dew is deposited. Analysis of the condensed liquid shows it to be equal quantities of hydrogen chloride, ferric chloride, and water.

It has been found in practice that, when cooling the product down to a temperature close to that of atmosphere, the corrosion on an iron pipe is not excessive. A standard 3-in. iron pipe lasted more than a year in practically continuous service. This was replaced by a double extra-heavy pipe, and life was greatly prolonged. The explosion diaphragm consisted of a rubberized asbestos disk protected from the heat by glass wool.

In many instances the gas leaving the burner at a temperature of 400°C. is satisfactorily cooled in passing through some lengths of iron pipe exposed to atmosphere. The cooling takes place through two gas films.

An alternative method of cooling is necessary when impure gas is used. Hydrogen chloride gas if impure can be safely cooled only to about 200°C. in iron pipe. With gas of this temperature the walls of the iron pipe exposed to the outside atmosphere are well above the temperature of dew deposition. Further cooling can be accomplished in equipment fabricated of impregnated graphite. This is a satisfactory method if muriatic acid is to be made.

However, if hydrogen chloride is required, an alternative method has been worked out which simultaneously cools and dries the gas. This is accomplished by passing the gas into a packed tower after it leaves the iron cooling pipe at a temperature in the vicinity of 250°. The tower can be constructed of iron. The gas is introduced into the center of the tower through a porous graphite or porous carbon pipe. It has been found the pipe can be jacketed with iron where it is outside the tower. The diffusion of moist hydrogen chloride through the graphite is insufficient to cause any serious corrosion.

The principle of submerged combustion can be applied very satisfactorily to the synthesis of muriatic acid. The burner and absorber are combined in the unit. The equipment consists of an acidproof tank, a rubber-lined steel tank with a brick lining over the rubber. The purpose of the brick is to keep the rubber cooler and to protect it from possible contact with the flame. The burner is constructed of graphite. Heat of combustion and of solution is removed by circulating the acid through a cooler. This cooler can be fabricated of impregnated graphite tubes, and the pumps can be of graphite, glass, porcelain, or olivite.

Salt Process.—In Hercules Powder Co.'s plant at Hopewell, Va., the acid is made by the salt process using a modified Laury-type furnace. Salt and sulphuric acid are fed in at one end of the rotary, oil-fired furnace, and the salt cake leaves at the other. Hot hydrochloric acid is removed by means of an electrically driven fan at the tail end of an absorption train. Hot hydrochloric acid gases are passed through a cyclone separator and thence through acidproof brick cooling towers and a coke-packed filter, where sulphuric acid mist is removed to absorption towers constructed of Haveg and impervious graphite. After purification the hydrochloric acid is used elsewhere in the plant.

The outstanding feature in this unit is the large volume of gas handled within a relatively small area by means of generous use of the synthetic resin and impervious graphite equipment.

A modern Mannheim hydrochloric acid unit at the Ethyl Corp.'s Baton Rouge, La., plant has been described. (Armstrong, *loc. cit.*) The operation is carried out in two stages: (1) the production of strong gas in the furnace and its absorption to make a concentrated hydrochloric acid and (2) the stripping of HCl gas from this concentrated acid.

In the first stage salt and sulphuric acid are fed into the Mannheim furnace, where, at a very high reaction temperature, sodium sulphate and a gas containing HCl diluted with air are yielded. The salt cake is drawn off and processed for sale, while the gas, under a slight vacuum produced by a blower at the top of the Haveg tails gas tower, is drawn into the absorption system.

The cooling of the hot, dilute furnace outlet gas is effected in a Knight tower, which consists of a steel shell with two courses of acidproof brick lining, the courses being separated by a 2-in. layer of glass wool. Plain raschig rings supported on a ceramic grid tile supply contact surface. This tower is resistant to a gas phase composed of air, hydrogen chloride, water, and low concentrations of sulphur dioxide, sulphur trioxide, and sulphuric acid. The liquid or cooling medium is a concentrated hydrochloric acid solution, containing a substantial amount of sulphuric acid, present in the tower at temperatures from 86°F. upward. This solution, which is heated by its passage down the tower, is cooled in cascade-type coolers composed of double banks of Karbate pipe and is recirculated by Karbate pumps to the top of the tower.

The absorption of the hydrogen chloride out of the cooled gas is effected principally in an impervious graphite cooler-absorber, with unabsorbed hydrogen chloride being removed from the exit gas in a Haveg tails tower before the gas is discharged to the atmosphere. Diluted hydrochloric acid enters the absorption system at the top of the Haveg tails tower, whence it flows to the top of the Karbate cooler-absorber after passing through double banks of impervious graphite cascade coolers. The tails tower is a Haveg shell with porcelain raschig rings supported on a Haveg grid plate.

As the cool, dilute hydrochloric acid solution passes down the cooler-absorber, it absorbs the hydrogen chloride and that part of the sulphur trioxide and sulphuric acid which has not previously been romoved from the gas stream in the Knight tower. The heat of absorption of the hydrogen chloride is removed by the circulation of cooling water through horizontal Karbate tubes which are an integral part of the cooler-absorber, in which the shell, tubes, tube sheets, distributor plate, and distributors are all impervious graphite.

This equipment must be able to withstand the action of warm hydrogen chloride gas (about 170°F.), of dilute hydrochloric acid at atmospheric temperatures, and of hot concentrated acid.

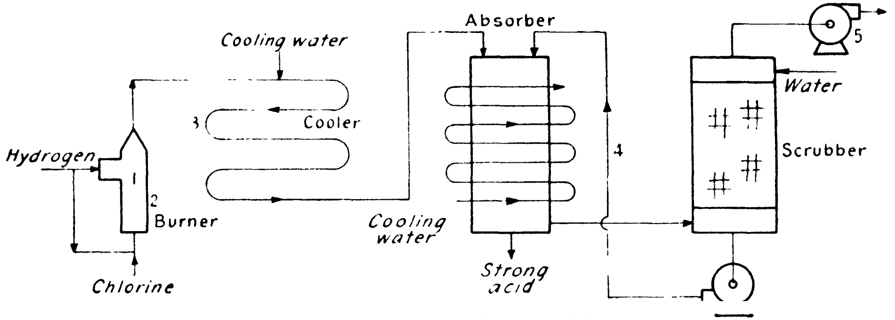
The concentrated hydrochloric acid solution from the bottom of the cooler-absorber is now ready for the final step of the operation, the recovery of a concentrated hydrogen chloride gas. This recovery is effected by pumping the solution to the top of an impervious graphite stripping tower, packed with 2-in. carbon raschig rings and connected to the bottom of one of two alternate, vertical impervious graphite reboilers. The stripped solution leaves the reboiler as a constant-boiling mixture of hydrochloric acid, sulphuric acid, and water which is cooled in Karbate cascade coolers and is then recycled to the cooler-absorber system. The overhead gas from the stripper passes through two identical, vertical, impervious graphite condensers, the condensate from which is recycled to the strippers. The gas from the condensers is now virtually pure hydrogen chloride, containing 0.3 to 0.5 per cent water, ready for the use in the manufacture of other chemicals.

In the stripper system, the stripping tower is constructed entirely of impervious graphite and is packed with 2-in. carbon raschig rings supported by impervious graphite grid plates. Neoprene gaskets are used throughout. The ends of the stripper sections have male and female connections, and the entire tower is spring-loaded to ensure tight joints with an equal differential expansion at all connection joints.

The reboilers are single-pass construction with Karbate tubes, tube sheets, and head covers and a steel shell and bottom head. Heat-transfer rates of approximately 550 Btu per hr. per sq. ft. per deg. F. have been obtained at steam pressures of 25 to 27 psi. gage. The condensers are single-pass construction and, like the reboilers, have a steel shell with Karbate tubes, tube sheets, and head covers. The pumps are Karbate units designed for a 100-ft. head.

The stripping tower operates at pressures of 5 to 8 psi. gage and at top temperatures of about 200°F., while the exit gas from the condensers is at approximately 120°F.

Synthetic Process.—The process of combining chlorine with hydrogen to make hydrochloric acid is simple and results in a very pure acid. (Badger, W. L., and E. M. Baker, "Inorganic Chemical Technology," 2d ed., p. 124, McGraw-Hill Book Company, Inc., New York, 1941.) The plant consists of a burner in which hydrogen burns in chlorine followed by an absorption system. This burner can be swung to one side, and the hydrogen ignited in the air. The burner is then swung under a sleeve, and chlorine is introduced so that the hydrogen burns in an atmosphere of chlorine, giving hydrogen chloride. Some installations use a large combustion chamber partly filled with broken refractory material and having an explosion vent, and some patents specify the use of an excess of hydrogen, which is collected at the end of the absorption system and returned to the burner. The simpler plant first described is, however, preferred in commercial operation.



Synthetic hydrochloric acid.

1. Silica nozzle
2. Silica, Karbate, brick-lined steel burner housing
3. Karbate
4. Haveg and tantalum, Haveg and Karbate, permanite and Karbate, Karbate; porcelain raschig rings in first and third combinations
5. Rubber-coated or phenolic-resin-coated steel

Acid is produced from this hydrogen chloride in much the same equipment as is used with Mannheim or Laury furnaces. The gas must first be cooled. Owing to the very high concentration of hydrogen chloride and the small percentage of inert gas, the absorbing system is relatively simple. In fact, with gas approximately 100 per cent HCl, absorption can be made complete in a few S bends or in a tantalum absorber without any scrubbing towers on the end of the system.

If water-white acid is to be produced, coke-packed towers cannot be used, since the coke contains enough soluble iron to color the acid strongly. Unglazed stoneware also will yield a colored acid, and even glazed stoneware will give up iron for a period of many months. The synthetic process, using a silica or tantalum absorption system, readily gives water-white acid.

By-product Hydrochloric Acid.—Many organic syntheses that are carried out on a large scale yield hydrochloric acid as a by-product. A typical example is the production of chlorbenzene. The gas coming from the equipment consists of hydrogen chloride, inert gas, and excess chlorine. This mixture is also saturated with volatile constituents, which, in the above case, are benzene and chlorbenzene. Before absorbing the hydrogen chloride, it is necessary to remove the benzene and chlorbenzene vapors. This is done by cooling to a low temperature, first in water-cooled lead coils and then by passing the gas up through a small packed tower countercurrent with refrigerated chlorbenzene. The gas remaining after this process is then sent to an ordinary hydrochloric acid-absorbing apparatus. The solubility of chlorine decreases rapidly as the concentration of hydrochloric acid increases, so that the finished acid does not ordinarily need to be treated to remove this dissolved chlorine.

Handling

Rubber.—Several manufacturers now line steel tanks for storage and shipping with vulcanized soft rubber, strongly bonded to the metal. Piping for cool acid is usually of hard rubber with screwed fittings. Properly supported, this will last many years, although a long line may present a different appearance in July and January. Rubber-lined steel has greater strength and lower thermal expansion but does not lend itself to quick repairs and changes, since it must be ordered from the factory in definite lengths. It is useful for conveying warm acid. (Graham, G. M., Hydrochloric Acid, *Chem. & Met. Eng.*, Vol. 41, No. 10, p. 524, 1934.)

Plug cocks of hard rubber, though far from perfect, seem the most practical value, although rubber-lined valves of the diaphragm type have shown encouraging results. Reciprocating pumps of hard rubber are fairly satisfactory, but centrifugal pumps of Durichlor possess certain advantages.

Rubber-lined steel also finds its place, as in exhausters, which show long life except for occasional recovering of impellers. With increased temperature, difficulty arises. Up to 80°C. hard rubber bonded to steel by means of a soft-rubber layer is very useful. Naturally, there is a temperature limitation on rubber.

For transferring HCl to various parts of the plant hard rubber, rubber-lined steel pipe, glass-lined steel pipe, and rubber hose are used. They give very satisfactory service. Agitators, centrifugal baskets, wash trays, and filter presses have given excellent service when made of hard rubber-covered steel.

Neoprene.—A neoprene-covered fan has shown a life of several years in a hydrochloric acid plant.

Koroseal.—Koroseal tubing has been used successfully to handle HCl in chemical-plant installations.

Tantalum.—A water-jacketed tapered tantalum condenser has found wide usage for condensation of HCl. Absorption plants, using tantalum heat-exchange surfaces, have been in operation for more than 11 years. The first unit was sold in 1937 and has been in continuous use. Tantalum has found its greatest usefulness from an economic viewpoint in processes involving HCl, HNO_3, and HBr, none of which attacks tantalum at any temperature or concentration obtainable at or near atmospheric pressure.

Tantalum heaters, usually of special design to keep gaskets out of contact with the acid, are used for distilling 20 to 22°Bé. muriatic acid. Tantalum condensers, also of special design, condense the constant-boiling acid vapor and remove the subsequent heat of absorption so that 22°Bé. acid is delivered from the condenser outlet. An aftercooler of Pyrex glass completes absorption of the HCl to make the product acid 23 to 23½°Bé.

Tantalum absorbers are used for muriatic acid where the HCl comes from organic chlorinations. They are satisfactory and economical as long as the HCl content of the by-product gas is 50 per cent or higher. Most of the food-grade acid sold is produced in tantalum absorbers.

Wood.—For low concentrations at ordinary temperatures wood can be used. Wooden tanks can be used satisfactorily for storing or processing of the acid up to 20 per cent and 212°F. Quarter-sawed cypress is generally considered the best material for this use. For higher concentrations it is necessary to treat the tank with pitch, asphalt, or paraffin.

Successful dryers have been made of wood heated with steam. The steam coils are not attached as long as they are hot enough so that the HCl vapors cannot condense on them.

Hydrochloric acid fumes readily, and since the fumes are so corrosive, provision must be made for their removal. Cypress coated with pitch, asphalt, or paraffin; high-silicon iron; and tile have all proved satisfactory for fume ducts. Wood, however, is generally most satisfactory.

In some cases wood tanks have been lined with rubber for storing the acid.

Hastelloys.—The wrought alloy Hastelloy A, which can be fabricated by all common methods, is superior to all other strong malleable materials in its resistance to HCl solutions under all conditions and in all concentrations and temperatures up to about 160°F. The cast alloy Hastelloy C is especially resistant to oxidizing acid-salt solutions.

Steel plug valves coated with Hastelloy B are used in hydrochloric acid service.

Chemical Stoneware.—This material is resistant to all concentrations and temperatures of the acid but has the disadvantages of high initial cost, poor heat transfer, and low mechanical strength. Acid pumps are usually made of stoneware or hard-rubber-lined steel. Stoneware is also used for transferring acid to various parts of the plant. Stoneware vessels are widely used for storage of HCl.

Carbon and Graphite.—Among the many applications of carbon and graphite equipment for the handling of hydrochloric acid are heat exchangers. The Bay Chemical Co. operating the Hargreaves process has installed an impervious graphite heat exchanger because of its high rates of heat transfer, great strength, and resistance to corrosive attacks. The gas leaves the producer at temperatures up to 800°F. and in concentrations in the order of 7 to 20 per cent HCl by volume. This gas must be cooled and the HCl dissolved in water to produce up to 20°Bé. muriatic acid.

Haveg.—One plant engineer reports that 20°Bé. HCl has been stored for the last 8 to 10 years in a Haveg tank. This replaced a steel tank lined with natural rubber which after 7 years had to be discarded, not because the rubber lining had failed, but because the steel in the tank itself had been corroded.

In an HCl plant Haveg is used for handling all gas. Pumps are nonstuffing box type made of Haveg with Hastelloy B trim. Values are made of the same materials.

Haveg vats are used for boiling solutions containing HCl. A vat has been in constant use for over 6 years on 10 per cent acid and has not shown any sign of attack. (McKillop, J., *Trans. I.C.E.*, Vol. 13, p. 63, 1935.)

Chlorimets.—Chlorimets 2 and 3 are said to be suitable for handling of all concentrations of hydrochloric acid. (Fontana, M. G., New Alloys for Severe Corrosion Services, *Chem. Eng.*, Vol. 53, No. 10, pp. 114–115, 1946.) Chlorimet 2 is used in many plants for handling solutions at various concentrations and temperatures. It is also extensively used for mixtures of HCl and organics.

Durichlor.—Centrifugal pumps of Durichlor are being used extensively in handling 30 per cent acid at temperatures from 30 to 40°C. (Mellen, W. W., and A. P. Smith, *Trans. A.I.Ch.E.*, Vol. 38, p. 831, 1942.) This is one of the most widely used alloys for HCl.

Teflon.—A composition of Teflon particles and graphite has proved satisfactory for packing. In view of its resistance to erosion and corrosion, Teflon has been tried in steam jet exhausters operating on steam at 150 psi. The exhausters are used to pull a vacuum on systems containing HCl vapors and free chlorine. Their performance has been outstanding. (Yelton, E. B., *Chem. Eng. Progress*, Vol. 44, No. 1, p. 89, 1948.)

Saran.—Saran-lined steel pipe is used for acid of 34 per cent up to 80°C. and for 36 per cent at atmospheric temperature. Other concentrations and temperatures at which Saran pipe is being used are 20 to 35 per cent at atmospheric temperature, 20 per cent at 170°F. and for boiling HCl and fumes up to 110°C. An engineer reports using Saran siphons and short pipe lines. Its only shortcoming he has noticed is that it becomes brittle at elevated temperatures.

Coatings.—Both phenolic and vinyl copolymer coatings can be used.

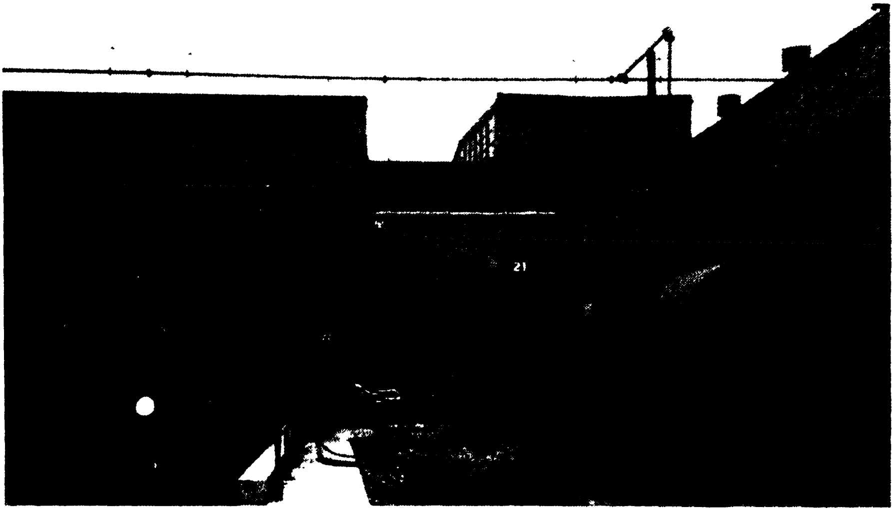
Acidproof Brick.—Hot HCl gases are passed through a cyclone separator and thence through an acidproof brick cooling tower and coke-packed filter in one chemical plant. Numerous other uses are made of acidproof brick in the handling of hydrochloric acid.

Fused Silica.—Burners, combustion furnaces, S-bend coolers, and absorption vessels are used for HCl gas and muriatic acid. The properties of impermeability, freedom from iron, resistance to thermal shock, and inertness to HCl have made fused silica of practical importance in production of HCl.

Copper.—High-copper alloys containing 1 to 5 per cent silicon and from 1 to 2 per cent manganese, tin, or iron have a notable feature in giving resistance to the action of HCl. All strengths of the cold and hot acid up to 20 per cent at 100°F. are handled satisfactorily in the absence of steam or air.

Copper with phosphorus and tin is a good metal for pumps, valves, and fittings used in contact with HCl up to 100°C.

Worthite.—Equipment of this alloy is being used with 15 per cent acid at room temperature. Worthite pumps are widely used for chemical descaling of steel equipment with dilute inhibited muriatic acid.



Hydrochloric acid may be shipped in rubber-lined tank cars and transferred in rubber hose. Other materials are also used for shipping and handling this acid.

Glass.—Glass pipe is used for transferring acid to various parts of the plant. Glass pumps are in use handling HCl.

Glass-lined Steel.—This material has the advantage over some materials of light construction and is practically indestructible from acid corrosion regardless of temperature and concentration. It is widely used for hydrochloric acid at all concentrations, especially since it can be fabricated as jacketed designs suited to heating, cooling, and agitation.

Chemical Porcelain.—This material is used for pipe lines transferring acid around the plant.

Nickel and Alloys.—Nickel is slightly superior to Monel in air-saturated acid under 10 per cent concentration by weight at atmospheric temperature and slightly inferior in air-free acid of any concentration and in air-saturated acid over 10 per cent concentration. Rates of corrosion increase uniformly with the acid concentration. At elevated temperatures, corrosion increases rapidly, and as a general rule, the use of Monel and nickel in hydrochloric acid at temperatures over 120°F. is confined to acid under 2 per cent.

Inconel possesses fair resistance to corrosion by hydrochloric acid. It has been found to be very satisfactory for handling mixtures of organic solvents with dilute hydrochloric acid.

Lead.—For handling hydrochloric acid, the use of lead is not generally recommended, but at normal temperatures there is only slight corrosion in concentrations up to 30 per cent, and at 212°F. concentrations as high as 20 per cent have been used.

Packaging

Among the containers used are the following: GR-S or natural-rubber-lined tank cars, wooden boxes with glass or earthenware inside containers, rubber-lined metal barrels or drums, rubber drums, wooden barrels or kegs with glass or earthenware inside containers, carboys in boxes or kegs, rubber-lined wooden barrels or kegs, and asphaltum-lined wooden barrels or kegs.

HYDROCHLORIC ACID—CARBON TETRACHLORIDE—BROMINE

Saran-lined steel pipe is in service handling weak bromine vapors, carbon tetrachloride, and weak hydrochloric acid.

Glass-lined steel can be used for all concentrations and at elevated temperatures.

HYDROCHLORIC ACID—HYDRAZINE HYDROCHLORIDE

Saran-lined steel pipe is said to last 20 times as long between 20 and 90°C. as copper pipe. In this particular case it was a 2.5-in. line from a reactor to the coolers.

HYDROCHLORIC ACID—NITRIC ACID—SELENOUS ACID—SULPHURIC ACID

Chlorimet 3 shows excellent resistance to a scrubber solution consisting of a mixture of sulphuric acid, hydrochloric acid, nitric acid, selenous acid, and sodium chloride at 140 to 150°F.

HYDROCHLORIC ACID—PERCHLORATE

Saran-lined steel pipe is in use for handling a 22 per cent solution of hydrochloric acid and perchlorate.

Glass-lined steel can be used for all concentrations and elevated temperatures.

HYDROCHLORIC ACID—SULPHURIC ACID

Tantalum coil is in use for boiling solutions. A Karbate centrifugal pump has been in service for 5 years handling "bug juice," a mixture of 7 per cent H_2SO_4 and 30 per cent HCl used for the knockdown scrubbing of HCl gases from Mannheim furnaces. (Palmquist, W. W., *Chem. Eng.*, Vol. 55, No. 6, p. 232, 1948.)

HYDROCYANIC ACID

Hydrocyanic acid is produced by several methods. In many cases it is made by the action of sulphuric acid on sodium cyanide. The Germans are reported to have been producing it from methanol, ammonia, and carbon monoxide. This acid is produced in the United States by the direct synthesis from natural gas, ammonia, and air and from sodium cyanide and sulphuric acid. HCN is not corrosive, but the acids used in its production and for stabilizing purposes give much trouble.

Production

Materials of Construction (H_2SO_4 and NaCN Process).—The generator and much of the other equipment are constructed from lead, Monel, or aluminum so as to prevent corrosion due to the dilute sulphuric acid used in the process. Copper is used extensively in other parts of the process. Aluminum is used for the rectifier section of stills, the reflux condensers, the final condensers, and mixing and filling tanks. It is also used for piping, rectifier columns, and various types of tanks.

Materials of Construction (Methanol, Ammonia, Carbon Monoxide Process).—The reaction vessels are of stainless-steel construction, while aluminum equipment is used for distillation as in the case of the first process.

Materials of Construction (Natural Gas, Ammonia, Air Process).—Types 304, 309, 310, and 316 stainless steels are all used extensively. For low-temperature service where there is practically no corrosion but where it is necessary to avoid contamination, Type 304 stainless is used. Type 316 is used for towers and piping handling moderately corrosive materials. Types 309 and 310 stainless steels are used for higher temperature applications.

Where sulphuric acid solutions might cause considerable trouble, lead or lead-lined equipment is in use. Worthite and Durimet 20 are used for pumps and valves throughout the plant.

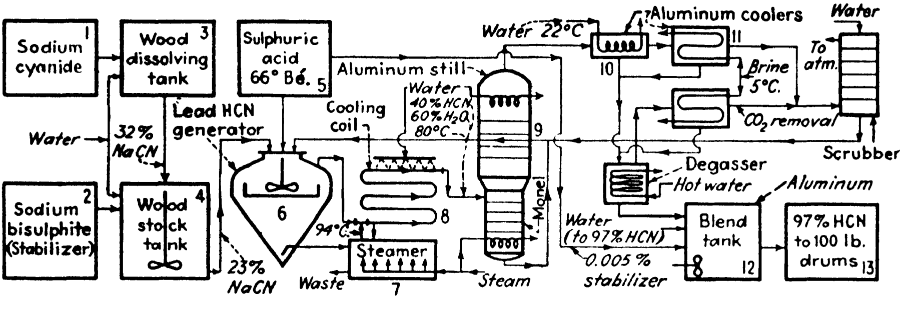
H_2SO_4 and NaCN Process.—Cyanide is dissolved in a steel cylindrical tank equipped with a perforated steel basket. Tank covers are wood. The solution is transferred by an all-iron centrifugal pump to a stock tank where it is diluted. It is pumped to a feed tank from which it flows to a HCN generator. (Carlisle, P. J., Manufacturing, Handling and Use of Hydrocyanic Acid, *Trans. A.I.Ch.E.*, Vol. 29, p. 113, 1933.)

The 66°Bé. H_2SO_4 flows from a steel storage tank to a cast-iron egg and is lifted by air pressure to steel feed tanks. The acid then flows to the HCN generator.

In the generator all internal surfaces are covered with antimonial lead. The mixer consists of a steel funnel. Supported near the top of the funnel is a lead mixing basin. To the periphery of the basin is fastened a lead apron. Cyanide and acid solutions are fed through lead pipes. As the solution flows down the wall of the funnel in a film, about 80 per cent of the HCN is liberated through a lead vapor-outlet pipe. The solution leaves the funnel and flows to the steamer, which removes the remainder of the HCN.

The steamer consists of a lead-lined, steel trough. Steam is admitted through lead pipes in the bottom of the trough.

All vapor piping from the generator to the stills is antimonial lead. The vapor pipes from the mixer and steamer enter a manifold which carries the vapors to a lead pipe cooler. Leaving the top of the cooler the enriched HCN vapor enters a separator—where some liquid is separated and returned to the inlet end of the steamer—and then passes to a still.



Liquid hydrocyanic acid.

1. Steel
2. Steel
3. Wood or steel with wood covers
4. Steel or wood
5. Steel
6. Hard lead-lined
7. Lead-lined steel
8. Lead
9. Monel lower section; copper coil, aluminum cups and aluminum upper section
10–13. Aluminum

The exhauster section of the still below the feed inlet is made of Monel. The boiling section proper is equipped with a copper steam coil. The rectifier section above the feed consists of seven plates with 22 aluminum cups per plate. The rectifier section is made up of seven cast-aluminum sections. Mounted directly above the rectifier section is an aluminum reflux condenser containing aluminum tubes. The condenser is capped by a cast-aluminum dome.

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

Vapors escaping the brine condenser pass to a water scrubbing tower where the last traces of HCN are removed.

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

Liquid HCN is allowed to accumulate in an aluminum tank. Here the 97 per cent product is slightly acidified with H_2SO_4, which acts as stabilizer. It is then pumped to an aluminum storage tank. Brass measuring tanks are used to fill the steel drums, which are heavily tinned inside and outside.

Methanol, Ammonia, Carbon Monoxide Process.—The I.G. Farbenindustrie plant at Oppau was the only plant of its kind in Germany producing hydrocyanic acid from the interaction between these three chemicals. [Boundy, R. H., and R. L. Hasche, Technical Report on Manufacturing of Miscellaneous Chemicals, Combined Intelligence Objectives Committee, G-2 Division, SHAEF (Rear) APO 413, U.S. Department of Commerce.]

The following steps were involved in the process: (1) methanol reacted with carbon monoxide to form methyl formate, (2) this was reacted with ammonia to produce formamide, (3) formamide was dehydrated to hydrocyanic acid.

The first step was carried out batchwise in a stainless-steel-lined autoclave. Methyl alcohol was charged to the reaction vessel, and 1 per cent NaOH added as catalyst. The mixture was heated by a steam jacket to 100°C. Water gas was introduced until equilibrium was reached. The reaction mixture was discharged, and the ester separated from the unreacted methanol by distillation in aluminum equipment.

The reaction between the methyl formate and the ammonia was carried out batchwise at a temperature of 60 to 70°C. and pressure of 10 to 15 atm. The reaction required cooling. This reaction was carried out in an autoclave with a bonded stainless-steel lining.

Dehydration of the formamide was carried out in the vapor phase at 200 to 300°C. over an activated alumina catalyst. Gaseous ammonia was used as diluent. The HCN was washed from the diluent ammonia, and the latter recirculated. A 30 per cent solution of sodium cyanide was obtained.

Natural Gas, Ammonia, Air Process.—All three raw materials are first purified. (Lee, J. A., Hydrogen Cyanide Production, *Chem. Eng.*, Vol. 56, No. 2, pp. 134–136, 1949.) The streams are heated, metered at a definite pressure, and passed to the stainless-steel converters in which the reaction takes place with the aid of a platinum catalyst at a bright red heat. Gases from the converter are scrubbed to remove unconverted ammonia. They are then passed through a process compressor and an absorber in which the HCN is removed from the gas by means of a liquid absorbent. The rich solution of HCN from the absorber passes to a distillation column in which the HCN is distilled out at high purity and condensed.

Handling

Measuring tanks for hydrogen cyanide of aluminum alloys have been used for many years and are in excellent condition. For spraying plants in the field, tanks small enough to be carried on the shoulder of a man are constructed of a relatively thin-gage aluminum-alloy sheet. These tanks have been in service several years.

Monel pipe and fittings are used for conducting hydrogen cyanide in chemical plants.

Packaging

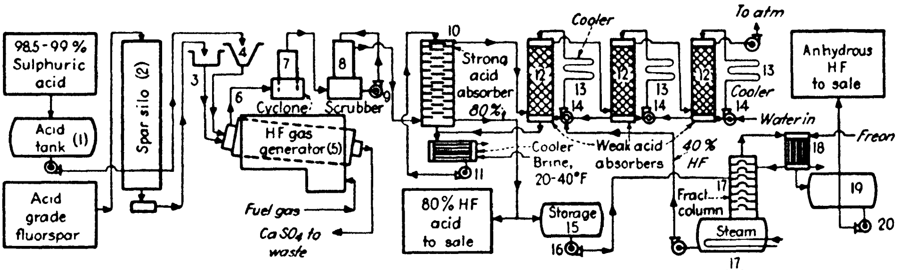
Hydrocyanic acid is shipped in steel cylinders, Monel drums, or aluminum containers.

HYDROFLUORIC ACID

The aqueous and anhydrous hydrofluoric acids behave differently toward materials of construction in both production and handling.

Production

Materials of Construction.—Most of the equipment is mild steel. Some lead, Karbate, copper, and other materials are used.



Anhydrous hydrofluoric acid.

1. Steel
2. Concrete
3. Steel
4. Steel
5. Mild-steel shell in brick
6. Steel
7. Steel
8. Steel
9. Lead
10. Steel
11. Steel
12. Carbon raschig-ring packing
13. Karbate
14. Karbate
15. Steel
16. Steel
17. Copper
18. Steel
19. Steel
20. Steel

Valves: Monel

Process.—Production of hydrofluoric acid in a plant completed in 1943 starts with the fluorspar. (Callaham, J. R., Fluorine Industry, *Chem. & Met. Eng.*, Vol. 53, No. 3, pp. 94–99, 1945.) It is stored in a silo and as required is transferred to steel, conical-bottom feed hoppers from which it is continuously fed to the still through an automatic scale and automatic feeder. Sulphuric acid of 98.5 to 99 per cent strength is fed through a rotameter into the still.

Furnaces have shells of mild steel enclosed in a brick setting. The retort rotates slowly. Calcium sulphate residue is discharged continuously. Gas consisting of 70 to 75 per cent HF is pulled off through a steel header at the feed end of the still at 250 to 350°F. After passing through a cyclone dust collector to remove spar carry-over, it is scrubbed countercurrently with condensed acid in a steel "scrubber acid" tower provided with a bottom receiver tank. Sulphuric acid entrained in the gas is removed and recirculated or bled back into the still. The circulating pump is of lead construction. Temperature of the gas is lowered to 150°F.

Gases from the still are pulled through into an absorption system consisting of a scrubber tower and overflow box, steel strong-acid-absorption towers, weak-acid-absorption towers, and pumps. Here the acid is concentrated to 80 per cent. The entire system is operated by a fan on the vent. The final product is run to steel storage tanks.

Strong acid is refrigerated in a brine-cooled shell and tube exchanger. Weak acid is cooled in conventional water-sprayed Karbate coils.

Strong-acid towers are plate and ring cascade type. Weak-acid lead towers, formerly of the cascade design, were replaced by carbon raschig ring packings. Strong-acid pumps are of mild steel, while those for acid under 80 per cent are of Karbate. Part of the weak acid is stored in neoprene-lined steel tanks and fed back to the absorption system.

Strong acid is stored in mild carbon-steel tanks from which it is pumped to the distilling column for concentration to anhydrous. This column is of copper construction. The copper reboiler is a kettle type with a bundle of copper tubes. Anhydrous acid leaving the still is condensed and cooled in a steel shell and tube condenser. The acid flows through steel lines to mild-steel storage tanks.

Monel valves are used throughout this plant and have given good service. Copper, used for the column and reboiler, is as satisfactory as any available material.

Handling

Both the aqueous and anhydrous acids will attack glass, concrete, and certain metals, especially those containing silicon, such as cast iron. They will also attack natural rubber, leather, and many organic materials.

Aqueous Acid.—Aqueous acid is a water solution of hydrogen fluoride, usually shipped commercially in concentrations varying between 30 and 80 per cent HF content. (Manufacturing Chemists Association, "Hydrofluoric Acid," Manual Sheet H-10, p. 3, 1948.)

Aqueous hydrofluoric acid at or above 60 per cent HF content can be handled and processed with the greatest assurance in piping and equipment made of Monel. Steel can be used alternately provided the concentrations of acid are such that internal passive surfaces of the steel will be preserved. Steel liners or equipment should not be flushed with water except for reasons of safety when repairs are necessary. Before using the lines or equipment for aqueous acid again, inner surfaces should be treated to restore the passive lining. (*Ibid.*)

Aqueous acid below 60 per cent HF content can be handled in Monel or lead lines. The preference is for Monel, since piping, fittings, and valves are available in standard sizes. Lead can be used in lines or equipment when the service of a qualified lead burner is available to make the installation and furnish proper maintenance. Flanged rubber-lined diaphragm valves can be used to regulate the flow of acid in a lead-line system. Steel lines must not be used for hydrofluoric acid below 60 per cent HF content.

Lines and equipment made of or lined with gum or ply rubber or neoprene can be used for hydrofluoric acid of 48 per cent content or lower. However, owing to the difficulty in obtaining standard fittings, rubber lines are not recommended for handling large quantities of acid.

Since the largest industrial applications include the use of hydrofluoric acid having 60 per cent HF content or higher, the following equipment is recommended for this class of service:

Piping: Extra-heavy seamless steel.

Fittings: Extra-heavy forged steel.

Unions: Forged-steel screw type with steel-to-steel seats, or forged steel flanges with gaskets.

Valves: Forged steel with outside screw and yoke.

Check valve: Forged Monel ball and body type.

Gaskets: If gaskets are necessary, it is optional to use soft copper, soft iron, soft silver, neoprene, Tauril, Vistanex-impregnated asbestos, polyethylene, polytetrafluorethane, or Saran.

Pumps: For aqueous acid, centrifugal pumps made of Monel, nickel bronze, or acid bronze (Cu, 87; Sn, 10; Pb, 3) can be used. Steel pumps are satisfactory for strengths of acid above 60 per cent HF content. (*Ibid.*)

One chemical plant has found a rubber pump satisfactory. Several pumps of rubber construction have been in operation 15 years. Yet another plant has turned to Karbate almost completely to handle dilute hydrofluoric acid. It has been found to be highly satisfactory.

Steel plug valves coated with Monel and with Stellite are used. Saran-lined steel pipe is used for aqueous acid of 30 to 70 per cent at 45°C. Other plants use Monel valves for dilute acid.

A fibrous form of Teflon has been developed that can be molded with a small percentage of binder to yield a packing ring suitable for high-speed pumps. Since the amount of binder required rarely exceeds 7 per cent, the chemical resistance of the packing ring is excellent. These packings have been used with excellent results on pumps handling hydrofluoric acid. (*Chem. Eng. Progress,* Vol. 44, No. 1, p. 89, 1948.)

For dilute-acid storage tanks neoprene-lined steel is in use.

An engineer writes that his company has experimented with a number of metals, finally concentrating on copper, Monel, and nickel, with emphasis on the first two at the present time. But the results have not been entirely satisfactory. Dilute acid is forcing the replacement with lines and equipment made with these metals every 6 months.

Another plant superintendent has brought out the fact that dilute acid (under 60 per cent) attacks steel but, if 1½ per cent sulphuric acid is added, it serves to pacify or protect the steel from corrosion.

Durimet 20 and Worthite can be used to handle hydrofluoric acid in concentrations below 10 and above 60 per cent at room temperature preferably when aerated. Chlorimet 3 pumps have been used for aerated HF, which corroded Monel, copper, and other alloys dependent on air-free solutions.

Karbate heat exchangers have been in use for several years. Karbate is easy to repair. Carbon cement makes any break or crack a comparatively minor matter, since a pump or line can be repaired in short order. In fact, Karbate is increasing in favor as a material of construction for handling dilute HF.

Silver and platinum are resistant to weak acids and are particularly useful for small parts or for special members such as frangible disks.

Anhydrous Acid.—Steel is the most widely used construction material for equipment in which anhydrous hydrofluoric acid is conveyed or processed. When equivalent in quality and strength, 18-8 stainless steel or Monel can be used. For centrifugal, rotary, or positive pressure pumps, steel or Monel metal is satisfactory.

Steel tanks are the logical storage vessels for HF and should be of welded construction conforming to paragraph U-68 of the A.S.M.E. code for unfired pressure vessels. Proper outage must be provided, and insulated storage tanks should not be loaded to more than 90 per cent of their water capacity—noninsulated tanks to 85 per cent. Where feasible, scale-mounted tanks are preferred to level indicators because of minimum error and trouble.

Extra-heavy seamless steel pipe and forged- or cast-steel fittings are preferable for handling HF. Welding makes the ideal joint, provided the weld is homogeneous and free of slag and oxides. Welded fittings should be used wherever possible. If threaded joints are used on small pipe, the threads should be carefully cut, pulled up tight and seal-welded. Some designers do not seal-weld pipe under 0.5-in. size, reporting threaded joints satisfactory. Some people caution against cast-iron fittings.

Needle, globe, and gate valves have been used successfully. Whenever application permits, a needle or globe valve is preferred because of its sturdy construction. Steel is an excellent construction material, and valves can be machined from bar stock or forged. Cast-steel valves, if used, must be carefully examined for porosity and sand holes. (Fehr, C. M., Materials of Construction for Anhydrous Hydrofluoric Acid, *Chem. & Met. Eng.*, Vol. 50, No. 11, p. 129, 1943.)

It was found by Fehr that because of its low corrosion rate mild carbon steel was excellent for storage tanks, pipes, fittings, valves, and pumps. This conclusion has been sustained by experience during the past 12 years, and it can be positively stated according to Fehr that steel tanks for storing HF have been in service for 10 years and are in good condition today.

Some steel is more resistant to anhydrous hydrofluoric acid than others. A thoroughly dioxidized, dead metal or killed steel in which the nonmetallic inclusions are absolutely at a minimum is the ideal steel. Bessemer steel is not desirable owing to lack of precise control.

Experience with Monel has been satisfactory, and it appears the best of all commercially available nonferrous metals for HF.

Copper has been found satisfactory in various parts of the process. Under proper conditions it is a close second to Monel. It is, however, attacked in the presence of sulphur dioxide and oxygen, and where these are present in the anhydrous hydrofluoric acid, copper is unsatisfactory. A copper coil put into operation in 1931 for 2 years and newly returned to service was recently examined. It was found to be in excellent state today. Copper tubing is very satisfactory especially where flexible connections are needed.

In addition to these metals, silver and platinum can be employed where the construction justifies. Platinum is probably the most resistant of all metals to HF, and silver has an excellent resistance in the absence of sulphides or appreciable quantities of sulphuric acid.

Packaging

Aqueous Acid.—Rubber drums of 5, 13, and 30 gal. are used for shipment of acid of not over 65 per cent strength. For strengths over 48 per cent, drums with special linings resistant to the ladings should be used. Acid of not less than 60 per cent and not more than 80 per cent strength can be shipped in carload or truck-load lots in unlined steel drums.

Rubber-lined steel drums are authorized by the I.C.C. for acid of strength not exceeding 62 per cent. The lead-lined drum is authorized where the strength of acid does not exceed 65 per cent.

Acid of not over 65 per cent can be shipped in boxed lead carboys and metal-jacketed lead carboys.

Acid not exceeding 30 per cent can be shipped in asphaltum-lined wood barrels.

Rubber-lined tank cars are authorized for acid not exceeding 40 per cent strength.

Wooden tanks when lined with asphaltum or other suitable material which will remain plastic and not be subject to destruction by the action of the ladings are authorized for acid of not over 30 per cent.

Unlined metal tank cars are used for acid of 60 to 80 per cent when the tanks have been subjected to adequate passivation.

Anhydrous Acid.—Shipment in seamless steel cylinders and in welded-steel cylinders is permitted. Shipment is also authorized in steel tank cars.

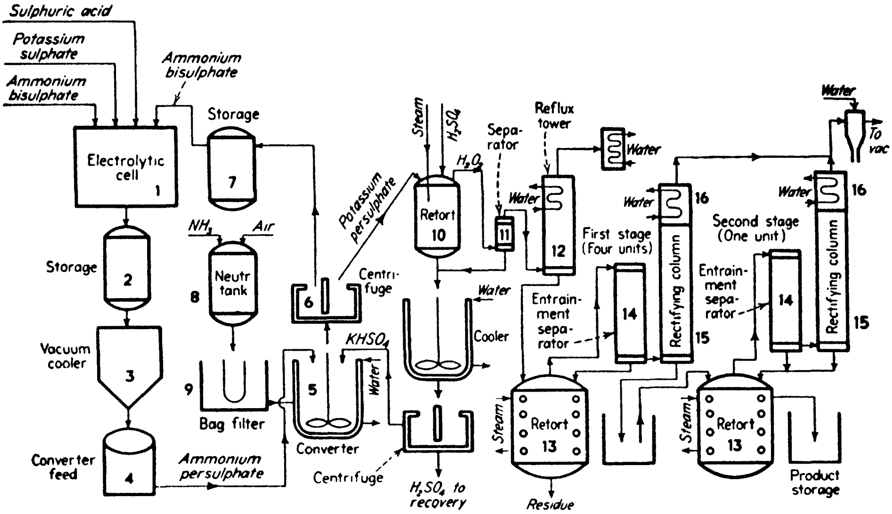
HYDROFLUORIC ACID—SULPHURIC ACID

It is for this service that the high-alloy stainless steel, Durimet 20, excels and is used in preference to high-silicon iron. The latter is not suitable for handling this mixture. Pumps of Durimet 20 are used by a chemical company to handle a solution containing 10 to 20 per cent sulphuric acid plus 1 to 5 per cent hydrofluoric acid at 120 to 140°F. (Luce, W. A., *Chem. Eng.*, Vol. 55, No. 6, p. 223, 1948.)

HYDROGEN PEROXIDE

Success in manufacturing, shipping, and applying hydrogen peroxide solutions in commercial uses depends largely on the selection of proper structural materials for processing equipment. Use of improper materials may lead to corrosion of equipment and also to accelerated decomposition and waste of hydrogen peroxide. Structural materials for handling and applying peroxide solutions must be considered a special problem for each particular set of conditions. One material which performs very satisfactorily under one set of conditions may prove entirely unsuitable under other conditions.

From comprehensive studies of the various metals and nonmetals to determine their resistance to the corrosive action of hydrogen peroxide and also to determine the effect of these materials on the stability of hydrogen peroxide solutions, it is evident that very few structural materials are suitable for handling peroxide solutions under practically all conditions of manufacture, storage, and use. In most cases, it is the effect on the stability of the peroxide solution which is the governing factor in choosing compatible structural materials.



Hydrogen peroxide.

1. Stoneware tube, carbon blocks
2. Stoneware
3. Stoneware and glass
4. Stoneware
5. Stainless steel
6. Stainless steel
7. Stoneware
8. Stoneware
9. Vinyl copolymer
10. Stoneware
11. Stoneware
12. Aluminum coil in stoneware
13. Stoneware with stainless-steel coil (Cr, 17.5; Ni. 12.5; Mo, 4.7; C, 0.07)
14. Aluminum
15. Stoneware
16. Aluminum

Production

Materials of Construction.—The materials generally favored for use in the production of hydrogen peroxide are glass-lined steel, stoneware, aluminum, glass, and stainless steel. Materials used in one plant for the fabrication of each piece of equipment are indicated in an accompanying diagrammatic flow sheet. The

Germans were partial to a stainless steel of the following composition: Cr, 17.5; Ni, 12.5; Mo, 4.7; C, 0.07 per cent.

Process.—Dilute hydrogen peroxide can be made by any one of several processes. This dilute material can be converted to high-strength product by distillation. Little has been published about the materials of construction used by American producers. However, a report (Bretschger, Crewson, and Cushing, German Hydrogen Peroxide Industry, PBI 7331, U.S. Department of Commerce, 1946) gives information on materials used by the Germans at Bad Lauterberg and at Hollriegelskreuth, where the Pietsch-Adolf potassium persulphate process was in use. A condensation of the report appears in *Chemical Engineering,* Vol. 55, No. 8, pp. 102–107, 1948.

The Hollriegelskreuth operation may be divided into four steps: electrolysis, conversion, hydrolysis, and concentration. Electrolysis of a solution of ammonium bisulphate in presence of potassium sulphate and sulphuric acid is carried out in a stoneware electrolytic cell. Cathodes are graphite rods. The electrolyte is collected in stoneware storage tanks, then pumped through a stoneware and glass vacuum cooler. It is next pumped to converters fabricated from stainless steel (Cr, 18; Ni, 8; Mo, 2.2; C, 0.07 per cent). Solid potassium bisulphate is added to the solution to precipitate potassium persulphate.

From the converters the $K_2S_2O_8$ slurry is pumped to an 18-8 stainless-steel centrifuge. Mother liquor is drained to stoneware storage tanks, where it is standardized for reuse as cell feed.

Solid potassium persulphate salt from the centrifuges is carried by belt conveyor and overhead trolleys to the hydrolysis equipment. A batch is charged into a stoneware retort, and sulphuric acid and live steam added. Vapors pass from the top of the retort through a stoneware entrainment separator and into a rectifying tower (aluminum coil in stoneware). Aluminum reflux condensers are built in the top. Average concentration of the rundown, which is the product, is 35 per cent. This is standardized in storage tanks and sent to the high-concentration plant.

Vapors from rectifying towers are caught by surface condensers (aluminum coils in stoneware columns).

The 35 per cent hydrogen peroxide is fed to stoneware retorts with a coil made of stainless steel (Cr, 17.5; Ni, 12.5; Mo, 4.7; C, 0.07 per cent).

Vapors from the retorts pass through aluminum separators for entrainment removal. They contain porcelain raschig rings. Next the vapors go to a chemical-stoneware fractionating column containing porcelain raschig rings. Aluminum reflux condensers are built into the top of the towers. The distilled, semiconcentrated product from the first, or purification, stage is withdrawn from the bottom of the rectifying tower.

For the second, or concentration, stage identical equipment is used, except that the rundown from the rectifying column is returned to the retort and the final product withdrawn from the retort. After leaving the retort of the concentration stage, the product is cooled in a double-pipe, stainless-steel (Cr, 17.5; Ni, 12.5;

Mo, 4.7; C, 0.07 per cent) cooler and then held in aluminum tanks for shipment. It is handled by stainless-steel pumps, aluminum piping, and stoneware valves.

Handling

Pure solutions of hydrogen peroxide are inherently very stable. When carefully purified and kept in clean, unreactive containers, the rate of decomposition is extremely slow. In general, the stability of very pure hydrogen peroxide increases with the concentration.

Decomposition into water and oxygen is accelerated by a wide variety of catalysts. Among the more active and commonly encountered catalysts are lead, manganese, copper, and iron. A slight trace of catalytically active material (parts per billion) will noticeably accelerate decomposition. Obviously, under commercial operating conditions such minute traces of catalytic materials, ever present in the surrounding atmosphere and in the walls of containing vessels, cannot be kept from entering the hydrogen peroxide solutions. Catalytic decomposition can, however, be inhibited by adding certain stabilizers to the solution. To be effective, a stabilizer must completely deactivate the catalytic materials and must continue to function for the life of the peroxide.

In the following discussion by J. S. Reichert and R. H. Pete of the Electrochemicals Department, E. I. du Pont de Nemours & Co. (*Chem. Eng.*, Vol. 54, No. 4, pp. 213–228, 1947), each structural material is handled separately. Due attention is given to inhibitors along with a description of the conditions under which the various materials will perform most satisfactorily.

Aluminum.—Aluminum in contact with solutions of hydrogen peroxide is subject to two kinds of corrosion which must be inhibited or kept to a minimum. Uniform dissolving of the aluminum is kept to a minimum when the hydrogen peroxide is stabilized at the mid-point of the titration curve, or "neutral point." Corrosion is accelerated in both acid and alkaline solutions. The dissolving of aluminum by hydrogen peroxide at a pH below the neutral point is inhibited by pyrophosphate. The other type of corrosion which occurs, localized pitting, can be prevented by the addition of nitrates.

In order to prevent catalytic decomposition the aluminum should be 99.6 per cent pure and free from foreign matter, which may be embedded in the surface or included in the weld deposits. Before placing aluminum equipment in service it is necessary to pickle thoroughly with 35 to 42 per cent nitric acid in order to remove all surface impurities. This pickling operation is critical and must be performed correctly. A peroxide storage tank will improve with age; this conditioning or aging effect may possibly be due to the build-up of an oxide film by the peroxide.

Aluminum which is 99.6 per cent pure is being used for fabrication of shipping drums and storage tanks where contact with the hydrogen peroxide is over an extended period of time. For pipes, fittings, and tank cars where contact with the peroxide is for short periods, 99 per cent aluminum is acceptable. Gas welding on aluminum equipment should be done with an oxyhydrogen flame, using 99.6 per cent aluminum welding rods and a suitable flux. Shielded arc welding is being used satisfactorily with a 99.6 per cent aluminum welding rod without flux; argon and helium supply the shield.

Stainless Steel.—Chrome-nickel steels, such as 304, 347 (columbium stabilized), 316 (containing molybdenum), and 316 Cb (columbium stabilized and containing molybdenum), are very resistant to corrosion by hydrogen peroxide under a wide range of conditions, *i.e.*, neutral, acid, and alkaline. However, these alloys have a mild catalytic effect on peroxide decomposition and are not generally recommended for long-time storage of concentrated solutions. With strong solutions the loss in strength due to catalytic decomposition in stainless-steel containers is likely to be appreciable under average storage conditions. With more dilute solutions of hydrogen peroxide (8 per cent or less) stainless-steel containers have been giving good performance. Stainless-steel storage equipment should be pickled with nitric acid before use with hydrogen peroxide.

Stainless steel, with its excellent physical characteristics and its resistance to corrosion, is an excellent structural material for use with hydrogen peroxide solutions of strengths as high as 50 per cent (and possibly higher) when contact with the solution is of short duration, *e.g.*, in valves, pumps, and pipe lines. Stainless steel is also excellent for tanks and agitators for preparing dilute peroxide bleaching solutions and for tanks, vats, and other equipment for bleaching operations.

Tin.—Metallic tin is passive toward neutral and slightly acid solutions of hydrogen peroxide in concentrations up to 50 per cent and possibly higher. It is corroded by alkaline solutions. Corrosion of tin by alkaline peroxide solutions is inhibited by the addition of sodium silicate. However, commercial sheet tin frequently has particles of iron scale or rust embedded in the surface which, if allowed to remain, will accelerate decomposition of the peroxide. The limitations of the physical characteristics of tin restrict its use; however, tin is giving good performance in pumps, pipe lines, tank linings, and other equipment.

Tantalum.—Tantalum is a suitable structural material for use with hydrogen peroxide under a very wide range of conditions as far as peroxide stability and resistance to corrosion are concerned. It has the disadvantage of high cost. However, there may be conditions when its initial high cost is offset by satisfactory service over a long period of time.

Lead.—Under most conditions lead is susceptible to corrosion in contact with hydrogen peroxide. Lead is a very active decomposition catalyst in solutions where lead oixde can readily be formed. In lead equipment corrosion of the metal and catalytic decomposition are inhibited to some extent by addition of sodium silicate. Lead-lined tanks are being used successfully in the process for bleaching raw wool where sulphates are present to form lead sulphate instead of the catalytically active lead oxide.

Iron.—Iron equipment is satisfactory only under special conditions and then only with quite dilute alkaline solutions. Iron is subject to corrosion by hydrogen peroxide and is a fairly active catalyst for peroxide decomposition. When iron is properly conditioned, corrosion of iron equipment is negligible in dilute alkaline solutions in the presence of sodium silicate. Under these conditions iron equipment is giving excellent performance in many bleaching installations.

Copper and Copper Alloys.—Copper is a very active decomposition catalyst and is also subject to corrosion. Copper equipment is therefore unsatisfactory under practically all conditions. Brass and bronze, like copper, do not give good performance. In some cases the copper in alloys does not act as copper, and its catalytic effect is not so pronounced. Monel, which contains 30 per cent copper, is being used successfully for some textile-bleaching operations.

Rubbers, Plastics, and Coatings.—Most ordinary rubbers do not give satisfactory performance in contact with high-strength hydrogen peroxide. The peroxide solution causes deterioration of the rubber and thus limits its useful life. The deterioration of the rubber is accompanied by acceleration of peroxide decomposition. Rubber hose has been used for dilute alkaline peroxide solutions, but the useful life of the hose is shortened to a period of 1 to 2 years. Natural rubber, as well as some synthetic rubbers such as neoprene, can be specially compounded for use with hydrogen peroxide.

There are a few plastics which can be used for tubing and gasket material with dilute and concentrated hydrogen peroxide; among these are some of the polyvinyl chlorides, Teflon, and polyethylenes. In general, coating materials are not satisfactory for use with concentrated hydrogen peroxide. The failure of most coating materials is due to the penetration of the peroxide through the coating to the base container, where gas bubbles peel off the coating.

Paraffins of the saturated hydrocarbon type have no catalytic effect on peroxide decomposition, and they undergo no deterioration in contact with hydrogen peroxide. As a coating material paraffin is difficult to apply and lacks good adhesive properties. White asbestos impregnated with paraffin or silicone stopcock grease is recommended for valve- and pump-packing material.

Wood.—Wooden tanks and pipes made of cypress and pine are fairly satisfactory for dilute peroxide solutions under many conditions. However, even dilute peroxide solutions, especially at high temperatures and high alkalinities, swell and soften wood fiber, thus shortening the life expectancy of wooden tanks to 4 to 6 years. For most satisfactory use, wooden tanks should be constructed with a concrete or tile bottom.

Glass and Ceramics.—In the nonmetals group, glass-lined steel and ceramic ware are widely used for hydrogen peroxide production and storage equipment. They are not attacked by hydrogen peroxide, and when properly cleaned they have no adverse catalytic effect. Ceramic ware is giving satisfactory performance in storage containers. The fragile nature of these materials is the main limitation to their use with peroxide solutions. Acidproof tile tanks and tile-lined concrete tanks have been used very satisfactorily for the preparation and storage of bleaching solutions and also for bleaching tanks and vats. Acid- and alkali-resistant cement is recommended for construction of these tanks.

Transite and Concrete.—Transite tanks and pipes are suitable for use with mildly alkaline, dilute peroxide in bleaching processes, particularly when sodium silicate is present in the bleaching solution. No adverse reaction between Transite and peroxide has been encountered over several years' use under these conditions. Concrete, like Transite, is suitable for use with dilute, alkaline solutions of hydrogen peroxide, particularly in bleaching solutions containing sodium silicate. Concrete equipment has been giving very satisfactory performance under these conditions.

Transite and concrete are not recommended for use with high-strength hydrogen peroxide.

Packaging

Commercial distribution of hydrogen peroxide in glass carboys and aluminum (99.6 per cent pure) drums and tank cars for shipment is common practice.

HYDROGEN SULPHIDE

The corrosion of steel by gases containing traces of hydrogen sulphide has long been troublesome. The corrosion of pressure stills in the petroleum-refining industry is one of the principal sources of expense and danger caused by hydrogen sulphide.

Handling

Stainless steels, aluminum and its alloys, aluminum paint, aluminum bronze, Inconel, nickel, austenitic cast iron, chemical stoneware, glass-lined steel, and Karbate are among the materials used for handling hydrogen sulphide.

In the case of hydrogen sulphide, cast-iron valves with stainless-steel trim will give reasonable service. There are several other alloys which are inert to hydrogen sulphide, such as aluminum and Type 304 stainless steel. (Koch, A. J., Diaphragm Control Valves, *Chem. Eng.*, Vol. 54, No. 6, pp. 207–218, 1947.) Inasmuch as diaphragm control valves are readily available in the latter alloy, this would be the practical choice. As with any other corrosion problem, the resistance material should be selected on a practical basis.

Calorized iron, aluminum, and stainless steels offer excellent resistance under the extreme conditions encountered in the parts of cracking stills operating at high temperatures and pressures. (Cooper, A. H., Experience Dictates Construction Materials for Handling Corrosive Agents, *Chem. & Met. Eng.*, Vol. 36, No. 12, pp. 747–752, 1929.)

Worthite and Durimet 20 equipment is being used with hydrogen sulphide in aqueous solution. Hydrogen sulphide in water is being handled by an austenitic cast-iron pump. The safe operating temperature of Inconel is said to be 1000°F. Karbate can handle a water solution up to saturation at boiling.

Aluminum and aluminum alloys are very resistant to dry and moist hydrogen sulphide gases. For instance, a column constructed of aluminum alloy has been used for 10 years to remove hydrogen sulphide from weak ammonia liquor.

Most applications of Monel and nickel are at moderate temperatures. Upper temperature limit for the metals is 500°F. Monel is used for sucker rods, gas lift pumps, meters, and pump parts in production of high-sulphur crude oils. K Monel is used for drill collars.

HYDROXYQUINOLINE

Process.—This is made by a Skraup reaction on *o*-nitrophenol. Glycerin and *o*-nitrophenol are charged to the kettle and heated to 118 to 120°C. Sulphuric acid (96 per cent) is added in one lot, the temperature rising to 130 to 133°C., then 60 portions of *o*-aminophenol and 96 per cent sulphuric acid are charged in alternately over a period of 3 hr. The temperature rises to 144 to 147°C. and is controlled within these limits by timing the charges of *o*-aminophenol and acid. Higher temperatures result in a reduced yield. When the charging is complete, the batch is maintained for 4 hr. at boiling temperature. Owing to the formation of water, the temperature falls to 130 to 133°C.

The batch is cooled to 40 to 50°C. and blown onto ice (600 kg.) with sufficient water (110 l.) to permit of stirring. It is neutralized to a faint acidity with 30 per cent caustic (about 300 to 400 kg.), and the residual acidity removed by addition of soda ash (about 26 kg.), a procedure adopted to give better filtration. The temperature during neutralization should not exceed 40°C., otherwise the product (m.p. 73°C.) becomes lumpy and occludes too much water and sodium carbonate. The batch is then filtered and drained as thoroughly as possible.

Two batches of the crude are charged to a direct-fired, 100-l. iron still (iron is not very suitable; copper is better). Water is removed by heating up to 130°C. per 25 mm. This takes 7 to 8 hr., and the internal temperature rises finally to over 360°C. (Adams, D. A. W., and W. Baird, Some Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Service, U.S. Department of Commerce.)

ISOPENTANE

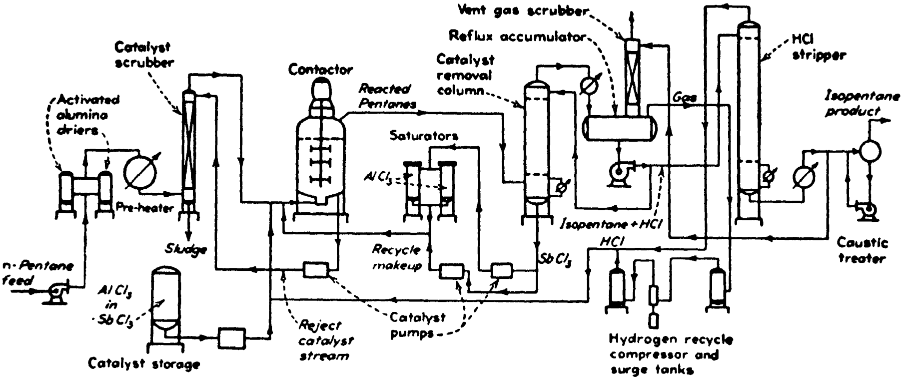
Since the latter half of 1944, Tide Water Associated Oil Co. has operated at its Avon, Calif., refinery a liquid-phase pentane-isomerization plant of the Shell type. This unit, the first commercial plant of its type, converts normal pentane to isopentane. (Galstaun, L. S., Isopentane Produced by Liquid-phase Isomerization, *Chem. & Met. Eng.*, Vol. 52, No. 9, pp. 109–111, 1945.)

Production

Materials of Construction.—No corrosion protection is required in vessels and lines in pentane service. Where pentane, catalyst, complex, and HCl must be handled together, carbon steel is satisfactory except in locations where turbulent conditions exist or in equipment such as motor and block valves where no corrosion is tolerable. The contactor is an example of a turbulent zone, and nickel-clad steel provides ample corrosion protection. All valves in catalyst service are of Hastelloy trim. In HCl-pentane service, carbon steel is entirely satisfactory and design is no different from that for similar services in butane isomerization.

Thermal or mechanical stresses in steel used for catalyst service generally cause an aggravated corrosion. Thus, stress relieving of large vessels or pipe in catalyst service is standard practice.

Process.—This plant is essentially similar to the liquid-phase butane isomerizers using antimony trichloride as a catalyst carrier which have been in commercial operation since 1942. A yield of 50 to 60 liquid volume per cent isopentane is obtained on a once-through basis. Side reactions are normally so slight that about 97 per cent yield can be obtained by recycling unconverted normal pentane. The flow is continuous as to both hydrocarbon feed and catalyst make-up.



Pentane. Ordinary steel and cast iron are satisfactory for vessels and lines in pentane service. Where pentane, catalyst, complex, and HCl must be handled together, carbon steel is satisfactory except in locations where turbulent conditions exist, or in equipment such as motor and block valves, where no corrosion is tolerable. The contactor is an example of a turbulent zone and nickel-clad steel provides ample corrosion protection. All valves in catalyst service are of Hastelloy trim. In HCl-pentane service, carbon steel is entirely satisfactory and design is no different than for similar services in butane isomerization. Thermal or mechanical stresses in steel used for catalyst service generally cause an aggravated corrosion. Thus, stress relieving of large vessels or pipe in catalyst service is standard practice.

Active catalyst employed is anhydrous aluminum chloride, together with 5 mole per cent of anhydrous hydrogen chloride. The aluminum chloride is carried as a solution in molten anhydrous antimony trichloride.

Normal pentane is pumped through dryers of activated aluminum. The feed then enters a preheater, and from there the dried feed runs to the catalyst scrubber column, where antimony trichloride and free aluminum chloride are countercurrently extracted from the reject catalyst stream entering at the top of this column.

The pentane stream flows to the contactor, where it is subjected to isomerization conditions. On the way, it passes through a manifold where recycle hydrogen, HCl, and antimony trichloride are injected as well as make-up aluminum chloride carried in antimony trichloride.

Reacted pentane mixture passes to the catalyst-removal column. The mixed pentanes, hydrogen, and HCl are distilled off as overhead product, while antimony trichloride containing aluminum chloride is separated as bottoms. The bulk of the trichloride is returned directly to the contactor by way of the catalyst recycle pump.

A small stream is pumped by the make-up pump through the saturators, where the trichloride dissolves aluminum chloride to supply make-up to the contactor. After passing through the saturators, the stream combines with the catalyst recycle stream and returns to the contactor.

Saturators are a dual unit and comprise two steam-jacketed pressure vessels. They are filled with anhydrous aluminum chloride.

Rate of aluminum chloride make-up is controlled by the rate of the make-up pump. This rate is set to maintain the aluminum chloride concentration in the contactor as required to obtain a satisfactory conversion.

Because of the large difference between the vapor pressures of the catalyst components and pentane, the catalyst-removal column has only ten trays and is operated at a reflux ratio of only 0.25 on the overhead. This is amply sufficient to obtain a clean separation between antimony trichloride and pentane.

The overhead portion is partially condensed, and the condensate is held in a reflux accumulator. Reflux for the catalyst column is obtained from the liquid in this tank. The bulk of the gas is recycled to the contactor by the hydrogen recycle compressor. The remainder is vented through a small vent-gas absorber, where hydrogen and light hydrocarbons are removed from the process and HCl and the heavier hydrocarbons retained. The light hydrocarbons are formed in small quantities as side products of the isomerization reaction and must be removed to prevent accumulation and a resultant pressure rise. The rate of venting is set to hold the pressure on the catalyst removal column within the controllable range. Cooled HCl-free product (obtained from the HCl stripper column bottoms) is used as "absorption oil." The bulk of the HCl is recovered from the vent gas by this means.

Accumulator liquid, comprising isomerized product and HCl, is pumped to the HCl stripper. In this column, HCl containing a small proportion of hydrocarbon is separated as an overhead product. This stream, in its entirety constituting the HCl recycle, is returned to the contactor. The bottoms are cooled and caustic-washed. This stream constitutes the entire plant product.

Operating surge for HCl is obtained in the HCl stripper. This column has 20 trays, and roughly the upper half is used as a surge tank for HCl. In this portion, the temperature is relatively low and the liquid holds sufficient HCl to absorb normal operating fluctuations in HCl flow. Below the surge portion the temperature rises sharply, indicating that the hydrocarbon is being denuded of HCl. By means of thermocouples on the trays, it is possible to determine how much of the column is available for HCl surge. Loss of HCl from the system is indicated by a rising level of the temperature "break." When this "break point" comes close to the top of the column, more HCl is added to the system.

Handling

Plain cast iron and steel can be used for handling isopentane, since no corrosion problems are encountered in vessels and lines in pentane service.

JAMS

Many different kinds of fruits and berries are used for making jam. Therefore the acids involved vary to some extent, resulting in varying needs for materials of construction.

Production

Materials of Construction.—Among the materials used for equipment are glass-lined steel, copper and its alloys, and silver.

Jam boiling pans are almost always made of copper and consist of a bell-shaped vessel fitted with an outer jacket also of copper surrounding the lower part of the pan to which pressure steam is admitted by cooking. An additional coil of copper tube is sometimes placed inside the pan to ensure rapid heating during the boiling operation. Pans may also be fitted with stirring gear made of bronze and with tilting arrangements instead of runoff cocks. For some purposes where volatile flavors are involved, the cooking is carried out in jacketed copper vacuum pans, which are fitted with covers with suitably arranged inlet and outlet valves. Jacketed copper vessels are also used for the preheating and cooking pans. (Cole, C. S., Copper, Brass and Bronze, *Food Ind.*, Vol. 7, No. 12, pp. 583–584, 1935.)

Among the pieces of equipment that are made of glass-lined steel is the vacuum pan.

Monel and nickel kettles are in use for boiling jams and jellies and for transfer buggies.

LACTIC ACID

Lactic acid gives the acid taste to milk that has soured. Its manufacture calls for sulphuric acid and naturally some special materials of construction. This acid is made by fermentation of any one of several raw materials: lactose in milk whey, dextrose from corn, and sugar in molasses.

Production

Materials of Construction.—The production of lactic acid is a relatively simple process; however, since lactic acid attacks most of the ordinary construction materials, some very formidable corrosion problems are encountered. Special materials are used for the heat exchangers, and the vacuum evaporators are either rubber- or glass-lined. The acid is finished to its final concentration in a glass-lined pot still. Ceramic valves and piping and Type 316 stainless-steel troughs and sheathing are used for handling and transferring the acid. Types 316 and 317 are used for evaporators in one plant. At another evaporators are made of Karbate and Hastelloy C.

Process.—Lactic acid can be produced from the fermentation of dextrose by lactobacilli. The fermenters are charged with dextrose, a nutrient, and powdered limestone and then inoculated with a lactobacillus culture. The $CaCO_3$ is present, so that, as soon as lactic acid is formed, it will be converted to calcium lactate. Otherwise, if the concentration of lactic acid were allowed to build up, the bacteria would destroy themselves before the reaction reached completion. The fermenter liquor is transferred to the acidulator, where sulphuric acid is added. This regenerates the lactic acid and precipitates calcium sulphate, which is subsequently removed by filtration. The dilute acid is concentrated to the desired strength and is decolorized with vegetable carbon.

Packaging

The finished acid is shipped in resin-lined or wooden tank cars, paraffin-lined barrels, and carboys.

LINSEED OIL

Linseed oil is not generally regarded as a corrosive material, and yet there are many applications for special alloys and other corrosion-resistant materials, both in its manufacture and handling.

Production

Materials of Construction.—Ordinary iron and steel and copper can be used for most of the equipment unless considerable free acid is present. For more corrosive conditions such metals as Monel, stainless steel, and aluminum are used.

For crushing cylinders, chilled iron can be used; for filters, cast iron, ordinary steel, or Monel; for piping, steel tubing, wrought iron, copper, Monel, or aluminum; for tanks, blue annealed steel, copper, Monel, or aluminum; for presses, low-carbon steel; for troughs, blue annealed steel, copper, Monel, or aluminum; and for processing kettles, steel, copper, or Monel.

Processes.—Linseed oil is made by any one of the several processes normally used for vegetable oils: hydraulic press, expeller, or solvent extraction. For a description of the processes see Vegetable Oils.

Handling

Preservation of the color of linseed oil for the varnish industry is an important factor in determining the choice of materials for boiling and bodying equipment. The oil contains a certain amount of free acids which attack iron, steel, copper, and some other metals, forming soluble soaps which darken the oil and simultaneously tend to increase the rate of formation of the acids themselves. (Anon., Preserving the Complexion of Linseed Oil, *Inco,* Vol. 12, No. 4, p. 20, 1935.) The problem has been solved by the adoption of Monel for kettles, mixers, shafts, agitators, and other parts coming into contact with the oil and varnish product. Inconel kettles are used for bodying linseed oil at 700°F. Inconel is also used on immersed electric heating elements.

Of course, the actual attack of the hot linseed oil on the equipment is not, even in the case of iron kettles, a particularly serious matter, but anything which increases the color of a clear varnish is definitely harmful to its salability. (Kellogg, D. R., Linseed Oil, *Chem. & Met. Eng.*, Vol. 41, No. 10, p. 524, 1934.)

Glass-lined steel vessels with electric heating elements housed in Monel have been used successfully for the high-temperature processing of linseed oil.

MAGNESIUM CHLORIDE

Magnesium chloride is made from magnesium carbonate, hydroxide, or oxide and hydrochloric acid. Also it is recovered from natural brines and from sea water.

Production

Materials of Construction.—A wide range of materials are used depending on the process and end use of the chemical. In one plant carbon steel is used for condensers, condenser tubes, crystallizers, dryers, evaporators, heat exchangers, piping, screens, and storage tanks. The same plant uses cast-iron crushers and grinders, filter presses, pumps, and valves and fittings. Kettles are brick-lined steel, with stainless-steel coils and Heresite-lined covers. Aging tanks are brick-lined steel.

Magnesium chloride is handled in this equipment made of tar-filled yellow pine and acidproof brick-lined steel, at the Dow Chemical Co.'s magnesium plant at Freeport, Tex.

In another plant Inconel is used for agitators, centrifugals, condensers and tubes, and screens. Heat exchangers are made of Inconel and 30 per cent nickel Ni-Resist. In the case of piping Inconel is used for hot liquors and ordinary steel for cold liquors. Pumps are Ni-Resist with Inconel trim. Inconel-clad steel is also used for some condensers.

Crystallizers are rubber-lined steel for solutions below 180°F. and brick-lined steel for solutions above that temperature. Dryers are brick-lined steel and Inconel. Evaporators are brick-lined steel bodies and Inconel tubes and heating elements. Tanks are brick-lined. Thickeners have Inconel mechanism in brick-lined steel tank.

Yet another plant uses glass-lined steel evaporator shells, heat exchangers, crystallizers, and tanks to prevent trouble from the hydrochloric acid.

Process.—The process used by Dow Chemical Co. to recover magnesium chloride from brines has been described under Magnesium Sulphate on page 208. At Freeport, Tex., Dow has a plant for the recovery of magnesium chloride from sea water. This chloride is used for the production of the metal. (Kirkpatrick, S. D., Magnesium from the Sea, *Chem. & Met. Eng.*, Vol. 48, No. 11, pp. 76–84, 1941.)

Sea water is treated with milk of lime in a concrete tank. The magnesium hydroxide is passed to steel thickeners. The flow goes to a Moore filter in a concrete tank. The hydrate is picked up by the filtering unit and carried to another compartment where air loosens the cake. This drops off, and a screw conveyor carries it to a neutralizing tank. Here in rubber-lined steel tanks, the hydrate meets the 10 per cent HCl solution which converts it to the chloride.

The dilute magnesium chloride solution is sprayed into a cylindrical brick-lined furnace. The steam, along with the products of combustion, passes through a steel tower and finally into one of asphalt-impregnated wood, where baffles remove the entrained water and solution.

A 35 per cent solution is tapped off the evaporator recirculating pump, forwarded to a vacuum cooler and thence to agitated, brick-lined retention tanks. This solution is evaporated to 48 per cent in brick-lined open-top kettles equipped with Type 316 or 347 stainless-steel heating coils. Great care must be exercised in stress relief annealing these coils and handling and installing them without strain in order to avoid stress corrosion. Final dehydration from 48 per cent solution to a granular solid is accomplished in a shelf dryer, which resembles a Herreshoff furnace.

Handling

Ordinary iron and steel are frequently used where a small amount of corrosion is not objectionable. Inconel-clad steel evaporators with tubes of Inconel are used successfully to concentrate dilute solutions. Durimet 20 is advantageous when solutions are hot and concentrated or when they contain impurities. Worthite too has been used successfully. High-silicon iron pumps are in use; also lead and stainless-steel pumps.

MAGNESIUM SULPHATE

This chemical is sold in several forms one of which is Epsom salts ($MgSO_4 \cdot 7H_2O$). It is used in dyeing and printing, for fireproofing fabrics, in chrome tanning, as a medicinal, and for many other purposes.

Production

Materials of Construction.—The use to which the magnesium sulphate will be put determines in some cases the materials of construction of the equipment. Some uses require a very pure product; other applications permit some impurities.

Cast iron is used for much equipment such as reaction kettles, pumps, and filter presses. Such stainless steels as 18-8 Cb and stabilized 18-8 Mo are used for evaporators, screens, and valves and fittings. Worthite equipment is in use. Durimet is completely resistant at all temperatures.

Monel is being used for crystallizers, extractor baskets, and dryers. It is also used for evaporators.

Ordinary steel has many uses including agitators, bins and hoppers, centrifugals, classifiers, condensers, condenser tubes, conveyors, crystallizers, dryers, filter presses, heat exchangers, piping, settling tanks, storage tanks, and thickeners.

Process.—Magnesium sulphate is produced by the action of sulphuric acid on the hydroxide or carbonate. The Dow Chemical Co. is making the sulphate from salt brines at Midland, Mich. (Gann, J. A., Magnesium Industry, *Trans. A.I.Ch.E.*, Vol. 24, pp. 206–225, 1930; and Badger, W. L., and E. M. Baker, "Inorganic Chemical Technology," 2d ed., pp. 199, 200, McGraw-Hill Book Company, Inc., New York, 1941.)

These brines are first treated to remove the bromine, then to remove traces of iron and then are evaporated to precipitate as much sodium chloride as possible. The salt is crystallized out, and the magnesium and calcium chlorides remain in the mother liquor. This mother liquor is concentrated in evaporators under such circumstances as to form the double salt tachydrite. This salt has the composition $2MgCl_2 \cdot CaCl_2 \cdot -12H_2O$. The brine being evaporated is richer in calcium chloride than in magnesium chloride, but tachydrite is richer in magnesium chloride than in calcium chloride. Consequently, the precipitation of tachydrite depletes the mother liquor with respect to $MgCl_2$ until it has been reduced to a ratio of $MgCl_2$ to $CaCl_2$ of 1:10. The tachydrite is dissolved in hot water, and the solution is cooled in continuous crystallizers. This produces crystals of substantially pure $MgCl_2 \cdot 6H_2O$. The mother liquor from these filters is returned to the tachydrite evaporators. Such small demands as there are for commercial magnesium chloride are supplied by the product of these tachydrite crystallizers, but by far the largest amount of $MgCl_2$ so produced is used for the manufacture of metallic magnesium.

The mother liquor from which the tachydrite crystals separate is then treated with lime to precipitate the magnesium as $Mg(OH)_2$. A very small amount of this $Mg(OH)_2$ is used for the removal of iron in the initial purification of the brine. The rest is treated with sulphuric acid, and the solution is crystallized in vacuum crystallizers to give commercial Epsom salts.

Handling

Steel and aluminum are satisfactory materials of construction for handling Epsom salts in either the dry state or in solution. Numerous iron, nickel, and aluminum alloys can also be used for this service. (E. I. du Pont de Nemours & Co., "Materials Handling for Groundwood Bleaching with Solozone.")

Monel is used for evaporators and heating coils or tubes handling magnesium sulphate. Cast iron, Worthite, and Durimet are used in handling.

Packaging

It is packaged in wooden barrels and kegs and in moistureproof paper bags.

MALTOSE SIRUP

A method for the production of maltose sirup from granular wheat flour has been developed. (Efron, A., and R. H. Blom, Production of Maltose Sirup from Granular Wheat Flour, *Ind. Eng. Chem.*, Vol. 40, No. 3, p. 412, 1948.)

The cooker used was a horizontal steel cylinder with a spiral agitator and several steam-injection fittings. The filter press had a top feed and an open discharge. Clarified liquors were concentrated in a glass evaporator operating at 25 to 27 in. vacuum, with steam at atmospheric pressure. The glass evaporator was similar to that of the long-tube vertical evaporators with natural circulation.

Flour and water were mixed in a pressure cooker. The pH of the mixture was adjusted to 5.5 with sulphuric acid, and the mixture was then heated to 126°C. with live steam. It was cooled to 65°C., and a slurry of malt and water was added. The sirup was then filtered and concentrated.

MEAT

Strict governmental controls and inspections of plants for processing beef, hogs, and other cattle, from killing rooms to sales coolers, have brought about extremely sanitary conditions. To obtain such cleanliness the packers have resorted to stainless steels and other modern materials of construction.

Production

Materials of Construction.—The larger and better equipped packing plants and other meat-handling places are using large amounts of stainless steels, aluminum, and other special materials.

Stainless Steel.—For many years stainless steel has served meat packers and retailers alike in numerous applications where absence of corrosion, ease of cleaning, and durable service are important. (Allegheny Ludlum Steel Corp., "Allegheny Metal in the Meat Industry," pp. 7–16.) The corrosion resistance of stainless steel makes it efficient in maintaining high standards of sanitation and bacterial control. Stainless ham molds were among the first applications and were forerunners of the table tops and meat hooks, tubing and mixers, viscera-inspection tables, conveyors, and trucks of stainless steel in today's modern meat industry.

In the killing rooms use is made of stainless-steel hooks. Head-inspection stands and flushing booths, head-trimming tables, trucks, trays and containers for edible parts, washing and shrouding equipment are stainless steel.

In the chill rooms, stainless-steel casing washers, belly rollers, and pork-cutting tables are used. Meat-cooler cases have recently been made with complete inside and outside containers constructed of 18-8 stainless-steel sheets.

Stainless-steel grinders, stuffing horns, and tables are often used in manufacturing pork sausage and other sausage specialties. Smokehouse linings and smokehouse conveyor rails of stainless give satisfactory service. Stainless ham and veal pans, when made of sufficiently heavy gage, contribute to long service life under severe conditions.

In the beef- and pork-dressing department stainless is used for viscera conveyors and viscera-inspection tables. Chutes, troughs, tanks, and vats used in beef, pork, and lamb dressing are fabricated of stainless steel. Meat trucks in many departments are made of this metal.

Sale cooler rooms in packers' plants and branch houses use racks, tables, and meat hooks of stainless for sanitary requirements and sales appeal.

Tin.—In handling meat products heavily tinned equipment is used to give a reasonable life without a heavy capital expense. (Gonser, B. W., Tin, *Food Ind.*, Vol. 7, No. 12, p. 585, 1935.) Among the applications for tin are galvanized-iron tables and other equipment where pickled pigs' feet are packed. Tinned-iron ham molds have long been in service.

Wood.—Tables and much other equipment in some packing plants, slaughterhouses, and retail butcher shops are made of wood.

Wrought Iron.—Some packers prefer wrought iron for meat cooking tanks.

Aluminum.—Equipment of aluminum alloys is used in the meat-packing industry. In the killing department, cans of aluminum alloys are used to store blood prior to its dehydration. In the canning department, steam-jacketed aluminum kettles are used for processing a wide variety of meat products prior to packing in glass or tin containers. Many items used to handle the different products between the different departments are made of aluminum alloys. These include smoke sticks, aluminum hand trucks, dish pans, and other types of containers. Aluminum pans are used for mixing spice and seasonings for the various products. They are also used for baking such products as meat loaf. In the canning department steam-jacketed kettles are used to prepare soup, and aluminum pails and pans are in use for holding large quantities of vegetables used in the preparation of the soups.

MERCURIC SULPHATE

Solutions of such salts as mercuric sulphate are highly oxidizing in nature and can be handled by Type 316 stainless steels for the hot solutions and Types 347 and 304 stainless steels and Inconel for more moderate temperatures.

The high-alloy stainless steels such as Worthite or Durimet 20 usually are resistant to these solutions under hot oxidizing and nonoxidizing conditions. These alloys are said to be superior to the 18-8 stainless steels owing to the presence of sulphuric acid in production.

Glass-lined steel is satisfactory at high temperatures and concentrations.

Chemical lead is not particularly affected by oxidizing or reducing conditions and in general has good resistance to most acid sulphate conditions.

METHYL ABIETATE

Methyl abietate is the methyl ester of abietic acid and is the principal constituent of Abalyn resin. (Lee, J. A., Hercules Makes Resins from Rosin, *Chem. Eng.*, Vol. 55, No. 11, pp. 129–132, 1948.)

Production

Materials of Construction.—The reactor is fabricated from stainless steel. Stills are copper construction. Much of the other equipment is made of black iron and ordinary steel.

Process.—Methyl abietate is made by the action of methanol on rosin at high pressure. Wood rosin is pumped from steel storage tanks by ordinary steel pumps to stainless-steel tube preheaters. Methanol, too, is preheated. The two preheated raw materials come together in a stainless-steel reactor. Rosin enters at the top and flows countercurrent to the methanol entering the reactor at the bottom. Conversion of the rosin to the methyl ester of abietic acid takes place at a pressure of 1,000 psi. The mass passes to the black-iron, crude-abietate feed pot.

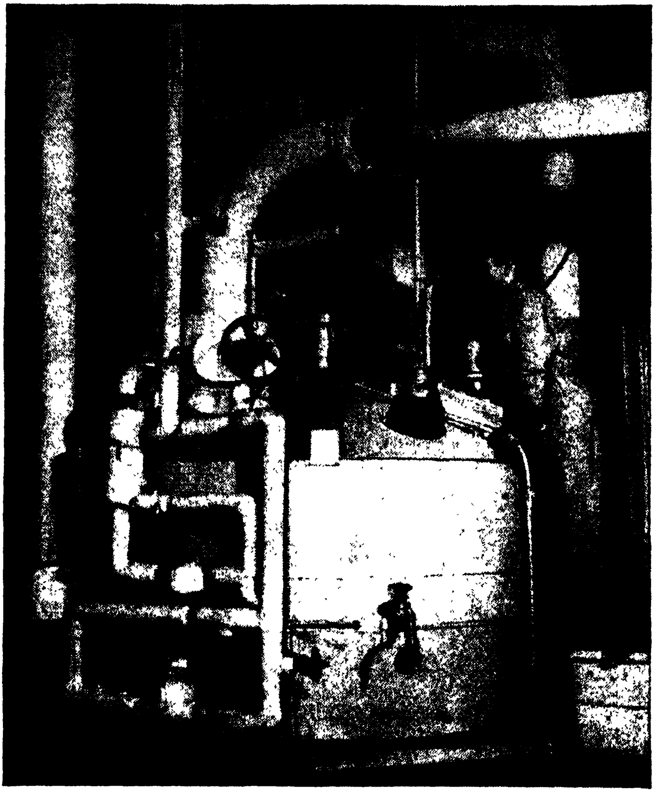
An excess of methanol is used in the reactor. The portion not consumed in the reaction passes to a copper still, where it is recovered. The crude product is vaporized and passes from the still to a steel separator. After separation, the refined material goes to a catch tank and from there to outside storage.

Packaging

It is shipped in steel tank cars to customers.

METHYL CHLORIDE

Several methods exist for the production of methyl chloride by the chlorination of methane. The process and materials of construction used by the Germans in the I.G. Farben. plant at Hoechst will be described. (Manufacture of



Stainless-steel kettles such as this one are being used to make a variety of different resinous products in Burlington, N.J., plant of Hercules Powder Co.

Methane Chloration Products in I.G. Hoechst Plant, FIAT Final Report 1299, Technical Industrial Intelligence Division, U.S. Department of Commerce, 1948.)

Production

Materials of Construction.—Cast iron is used by the Germans for the mixing vessel for methane and chlorine. The chlorination kiln wall bottom is made of Sichromal 8 (high-temperature-resistant alloy of Si, Cr, and Al). The upper part is ring-packed. The inner wall is concrete-lined. The kiln is lined with fireproof brick. Hydrochloric acid absorption towers are acidproof-brick-lined. Hostalit pipes and valves are used. In the United States Inconel heaters, reaction vessels, and piping are used in high-temperature chlorination of methane where temperatures are above the dew point.

Process.—Briefly, the process consists of mixing methane with chlorine in the ratio of 5:1. Mixed gases are transformed into methane chlorination products in a chlorination kiln in the presence of gaseous hydrochloric acid, carbon dioxide, and recycled methyl chloride. From the uncooled gases, hydrogen chloride is washed out by water at temperatures above the dew point of the chlorination products. Residual HCl and CO_2 are removed by absorption in alkaline solutions. Part of the caustic wash solution is transformed into a sodium carbonate solution which is used as a prewash. Final scrubbing is effected with caustic.

By means of refrigeration the washed and compressed chlorinated gases are then freed from moisture and liquefied in three steps: precooling, medium refrigeration, and low-temperature refrigeration. The liquefied chlorination products are purified by distillation, methyl chloride and methylene chloride by pressure distillation, and the chloroform and carbon tetrachloride by atmospheric distillation. Some methyl chloride is recycled.

Handling

Tantalum condensers are used in some plants in the United States to reflux methanol and hydrochloric acid to reactors, to keep the acid out of the drying and purifying equipment, and to reduce the loss of methanol. There is no corrosion of the condensers, and they provide continuous operation for long periods.

Methyl chloride under many conditions of exposure does not seem to have much action on aluminum. However, in the absence of moisture and in the presence of a catalyst such as aluminum chloride, methyl chloride attacks aluminum with formation of spontaneously flammable methyl aluminum chloride. For this reason the use of methyl chloride in contact with aluminum is not recommended. (Aluminum Co. of America, "Aluminum in Chemical Industry," p. 42, 1944.)

Glass-lined steel is entirely satisfactory for methyl chloride.

Worthite pumps and valves are being used to handle methyl chloride. All-cast-iron pumps are in use. Monel valves and strainers are used to handle methyl chloride in refrigeration applications.

A fibrous form of Teflon has been developed that can be molded with a small percentage of binder to yield a packing ring suitable for high-speed pumps. Since the amount of binder required rarely exceeds 7 per cent, the chemical resistance of the packing ring is excellent. These packings have been used with excellent results on pumps handling methyl chloride. (*Chem. Eng. Progress*, Vol. 44, No. 1, p. 89, 1948.)

Packaging

Methyl chloride is put into steel cylinders.

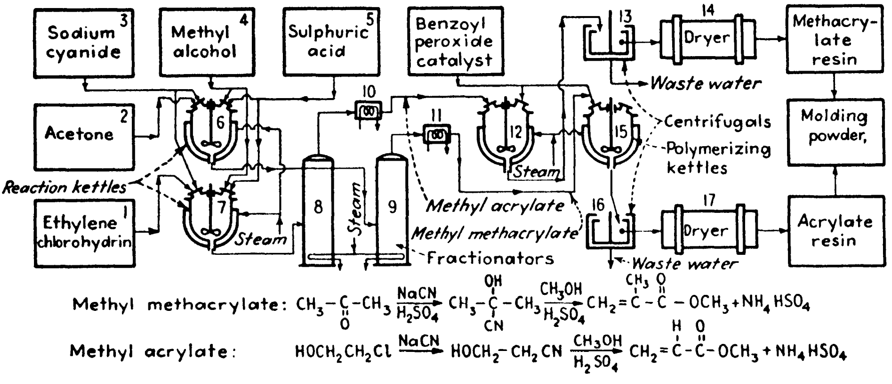
METHYL METHACRYLATE

Methyl methacrylate monomer was prepared from acetone cyanhydrin by Rohm and Haas at Darmstadt, Germany, during the last war, it has been reported by American investigators.

Production

Materials of Construction.—The acetone cyanhydrin was treated with sulphuric acid in glass-lined tanks. Much of the other equipment including the esterifier was brick-lined steel. The distillation equipment for the most part was made of aluminum. The finished monomer was stored in aluminum.

Process.—One mole of acetone cyanhydrin (98 per cent pure) was charged to a glass-lined tank, and 1.35 moles of concentrated sulphuric acid were then added slowly during a period of about 30 min., keeping the temperature at 60°C. A sirupy mass resulted. As soon as all the acid had been added, the mixture was heated quickly (20- to 25-min. cycle) to 128°C. in order to complete the formation of methyl acrylamide.



Methyl methacrylate: $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[H_2SO_4]{NaCN} CH_3-\underset{CN}{\overset{OH}{C}}-CH_3 \xrightarrow[H_2SO_4]{CH_3OH} CH_2=\overset{CH_3}{C}-\overset{O}{\overset{\|}{C}}-OCH_3+NH_4HSO_4$

Methyl acrylate: $HOCH_2CH_2Cl \xrightarrow{NaCN} HOCH_2-CH_2CN \xrightarrow[H_2SO_4]{CH_3OH} CH_2=\overset{H}{C}-\overset{O}{\overset{\|}{C}}-OCH_3+NH_4HSO_4$

Acrylic resins.

1. Glass-lined
2. Glass-lined, steel
3. Lead-lined
4. Lead-lined, steel
5. Lead-lined
6. Stainless steel
7. Stainless steel
8. Stainless steel, copper
9. Stainless steel, copper
10. Stainless steel, copper
11. Stainless steel, copper

12–17. Stainless steel

The amide product was then transferred to the esterifier, a vessel of 1,500-gal. capacity, equipped with a turbine-type stirrer of high-silicon iron construction. Next 1.8 moles of methanol were added, followed by water, which was added at such a rate that the heat of dilution plus the heat of reaction was sufficient to maintain the batch temperature at 80°C. Cooling was accomplished by refluxing methanol at the start of the reaction. During the one to one and a half operating cycle the esterification and hydrolysis reactions took place simultaneously to yield methyl methacrylate and dilute sulphuric acid.

The reaction mixture was then dropped to a brick-lined tank, and live steam was added to strip the volatiles from the sulphuric acid-ammonium sulphate residue. The distillate separated into an upper layer containing about 95 per cent methyl methacrylate plus water and methanol and a lower layer of methanol and water plus a trace of monomer. The lower layer was distilled batchwise to recover, in order, monomer, dilute methanol which was recycled, and a water residue which was discarded.

The upper layer was mixed with inhibitor using about 0.025 parts phenol per part of monomer and then distilled continuously in bubble-cap stills of aluminum construction, with the exception of the reboiler of the second still which was steel. The first column removed all the low-boilers overhead. This product was washed with water, the upper monomer layer was recycled, and the lower water layer was discarded. The second continuous column, operating at about 300 mm., delivered pure monomer. Experience had shown that high-purity monomer was necessary for the production of a quality polymer. Therefore, a minimum purity of 99.9 per cent was specified.

The residue from the monomer still containing phenol plus polymer was cracked at 350°C. in an electrically heated steel still. This unit, operating at atmospheric pressure, was equipped with a slow-speed scraper-type stirrer. Feed was semicontinuous. The monomer and the phenol together with monomer formed by depolymerization distilled off, leaving a carbon residue which was collected in a sump at the discharge end of the still. The overhead was recycled to the monomer purification system, and the coke residue was removed periodically.

Finished monomer was stored in aluminum tanks maintained at 0 to 2°C. A nitrogen atmosphere was not essential, and storage for a period as long as 5 months was not harmful.

MILK AND MILK PRODUCTS

Dairy products furnish an ideal medium for the growth of many groups of bacteria and thus require care and skill in their handling to assure a wholesome end product. (Information for this section from L. R. Glazier.) Local and Federal regulations and inspectors insist on sanitary, easily cleaned equipment maintained in proper condition. Plant operators and workers have been educated to disassemble all sanitary piping and equipment coming in contact with the product, during the daily clean-up period, so that it can be kept clean.

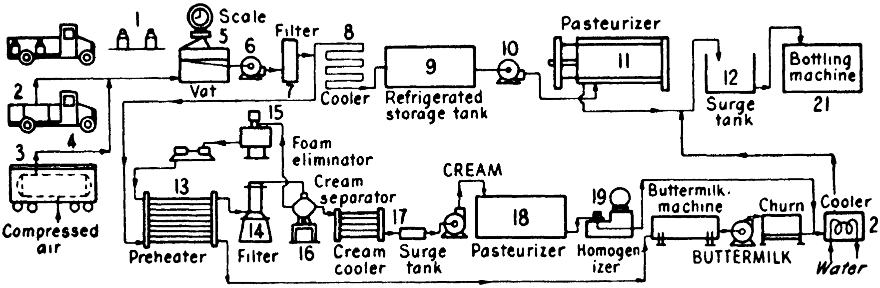
Production

Materials of Construction.—During the past several years stainless steel has replaced the metals formerly used, although one still finds considerable "dairy metal" or "white metal" (nickel alloys) in pipe and fittings, tank outlet valves, and sanitary milk pumps.

Stainless Steel.—Dairy plants are perhaps using stainless-steel equipment more extensively than any other branch of the food industry. It is quite generally used wherever the product comes in contact with metal. This is especially true in the case of the various types of milk coolers, storage tanks, truck and railway tanks, where the milk may stand for several hours. A high percentage of the batch pasteurizers are fabricated of stainless steel, as well as most flash or high-temperature units.

Other pieces of stainless-steel equipment in dairies include such items as vacuum pans, dump and weigh tanks, receiving tanks, filters, pumps, balance tanks, bottle fillers, ice-cream freezers, and the contact parts of many others such as homogenizers and packaging machines.

Where brine is used for cooling purposes, stainless steel should be avoided, except when the equipment can be readily taken apart daily for flushing down with water. An example of this is the plate cooler, where brine flows on one side of the plates and milk on the other. These coolers can be quickly opened and washed to prevent corrosion. Jackets of stainless-steel pasteurizers or holding tanks should not be flooded with brine, as corrosion will be a serious problem, especially in cases where the jacket is not left in a flooded state at all times.



Milk, cream, and buttermilk.

1. Stainless steel, aluminum
2. Stainless steel, aluminum, glass-lined steel, phenolic-resin-lined steel
3. Stainless steel, aluminum, glass-lined steel, phenolic-resin-lined steel
4. Aluminum, glass, stainless steel
5. Stainless steel
6. Stainless steel, tinned bronze
7. Stainless steel
8. Stainless steel, aluminum
9. Stainless steel, aluminum, glass-lined steel
10. Stainless steel
11. Aluminum, stainless steel, glass-lined steel, phenolic-resin-lined
12. Aluminum, stainless steel, glass-lined steel
13. Stainless steel, aluminum
14. Stainless steel, aluminum
15. Stainless steel, aluminum
16. Stainless steel, aluminum
17. Stainless steel, aluminum
18. Aluminum, stainless steel, glass-lined
19. Stainless steel, aluminum
20. Stainless steel
21. Stainless steel

Aluminum.—This metal was used to some extent in the construction of dairy storage tanks and subsequently for sheathing the exteriors of tanks, particularly truck tanks, and for paddle-type agitators. Some plate-type heaters, coolers, and filters have also been constructed of this metal. Because of corrosion and pitting of the metal when used in connection with other metals, it has been replaced a good deal by stainless steel. It is now used in limited quantities for milk cans and butter churns and in considerable amounts as aluminum-foil hoods for milk bottles.

Glass-lined Steel.—Many milk rail-transportation and truck tanks were formerly made of glass-lined steel, but these are being replaced with stainless steel because of the saving in weight. There are, however, many storage tanks made of this material that are still in use. This construction is also used for steam- or brine-jacketed equipment, including batch pasteurizers.

Glass.—A good deal of experimental work has been done by some of the glass companies and university experiment stations on the use of glass tubing to replace metal sanitary tubing for milk lines. Some dairies have installed such glass pipe lines. If board of health approval should be generally obtained so they need not be taken down for dairy cleaning, considerable economy of labor would be effected.

Tin.—Tinned equipment has been used in the dairy industry for years because of its relative ease in fabrication and comparatively low cost. There is no general attack on tin by sweet milk under normal conditions. Localized corrosion may be encountered in open containers, especially if the base metal is partly exposed or if the milk is held in the container for long periods. Black spots in tinned milk cans have frequently been caused by the farmer's leaving a stirrer of pure nickel or other metal superior to steel in the cans overnight. Electrolysis caused by the dissimilar metals and the lactic acid oxidizes the tin to form the uneven black spots.

Tinned copper was formerly the most common material used in the construction of milk equipment. This has been replaced to a great extent by stainless steel, although tinned-copper surface coolers are still available.

Nickel and Monel.—These metals are not considered entirely satisfactory for milk-handling equipment, as they are corroded by cooling milk. The alloys of nickel known as "dairy metal" or "white metal" have been extensively used for sanitary pipe and fittings, outlet valves, and milk pumps. As these contain copper, which is soluble in milk, some large dairies and dairy schools discourage their use in favor of stainless steel in order to prevent the development of oxidized flavors.

The alloy Inconel is resistant to corrosion by milk under all conditions and is recommended by some where resistance to corrosion by refrigerating brines is required. It should be pointed out, however, that most fabricators will make no guarantee of brine-cooled coils or jackets made of this material.

Coatings.—During the critical shortage period of the Second World War when stainless steel and glass-lined steel were unavailable, some mild-steel milk-storage and whey-storage tanks were coated with a phenolic resin protective coating. This and similar coatings were also applied to some truck tanks. In considering the use of a phenolic coating one should have the manufacturer's guarantee that no free phenol will be given off. Free phenol not only would affect the flavor of the product but would also be apt to give a positive phosphatase test.

Wood.—Although there are cast-aluminum butter churns on the market, the vast majority are still made of special woods.

Process.—It is beyond the scope of this chapter to go into detail in the processing of milk and its many by-products. Some idea of the various operations in a milk plant can be obtained by tracing the flow of product through a hypothetical plant handling such allied products as cream, cultured buttermilk, and condensed milk.

It is assumed that the milk arrives by truck in the usual 40-qt. cans. The cans are slid off the trucks onto a gravity or power conveyor and conveyed the short distance to the combination dump and weigh tank. This is mounted on scales which automatically show and record the weight of each farmer's milk.

The milk drops from the weigh tank to the shallow semirectangular receiving tank immediately below. From here it is pumped by a sanitary stainless-steel pump through a cold-milk filter (or clarifier) to the large insulated storage tanks.

The empty cans are placed upside down in the automatic can washer with the covers directly above in the upper section. As they emerge from the other end of this straight-through washer, the cans are automatically turned upright and the covers put in place. A conveyor carries the clean, sterile cans to the outside of the building ahead of the receiving conveyor, and the truck moves forward and loads on the empties, thus making room for the next truck in line to unload. Any rejected milk is returned to the truck by a separate short conveyor.

As the milk is required for processing, it is pumped from the storage tanks to the batch pasteurizers or through the preheater and final heating sections of the flash-plate pasteurizers. It is then pumped through or over a cooler to a surge tank supplying the automatic bottle fillers and cappers.

Milk which is homogenized is preheated and pumped through the homogenizer, preferably before pasteurization.

A continuous supply of clean bottles is conveyor-fed to the fillers from the automatic soaker-type bottle washer located in the returned-bottle room. An empty case washer is located adjacent to the bottle washer, and as the cases are emptied of their dirty bottles, the cases are conveyed to and through the case washer. Continuing on by conveyor they arrive at the filling machines to coincide with the speed of these machines to be filled with the full bottles of freshly pasteurized milk. As the cases are filled, they slide along into the large cooler rooms, where they are stacked until ready for delivery the following morning.

As some milk is required for cream sales, a portion is separated through a machine known as a "centrifugal separator." This centrifuges the milk so that the lighter cream comes out of the inner cream spout while the heavier skim milk moves toward the outside and thence out of the skim-milk spout. A temperature of 85 to 90°F. is usually recommended for separation.

Skim milk can be disposed of in one of several by-products, such as cottage cheese, cultured buttermilk, or plain condensed milk for bakery products or ice cream. The first two products are normally produced in a fluid-milk plant, while some have vacuum pans to handle their surplus.

That skim milk going into cottage cheese is pasteurized and cooled to 70°F., diverted to large open cheese vats, and cultured with a lactic acid bacteria culture. Following a 12- to 16-hr. incubation period, the cheese is cut, cooked, washed, drained, salted, and boxed for sale.

Skim milk for buttermilk is pumped into jacketed pasteurizers with cooling facilities, pasteurized to a temperature of 180 to 190°F., and cooled and cultured as in the case of cottage cheese. When the proper viscosity and acidity are built up, it is agitated and cooled for bottling.

The making of whole or skim condensed milk is similar, except that the degree of concentration is varied. Milk for canning is whole milk condensed approximately 2.25:1 so that it has a minimum of 7.8 per cent butterfat in the finished can. Skim milk can be concentrated as high as 4:1 to give a high solids product for use in ice-cream mixes, bakery products, or candies. The fluid milk is heated by continuous barrel heaters, plate heaters, or hot wells to approximately 165°F. (195 to 200°F. if sugar is added). It then is sucked into the vacuum pan by the existing vacuum and concentrated by boiling under a vacuum of 27 to 29 in. It can then be cooled through a continuous cooler and run into a storage tank to await drawing off into 40-qt. cans, or it can be drawn from the pan into jacketed condensed-milk cooling tanks.

The condensed whole milk that is retailed in small cans involves a much longer process following concentration. It is homogenized, standardized, canned, sterilized, and shaken.

Processing cheese, butter, and ice cream are specialties in themselves and entail fairly long procedures. Several books are written on each subject, and it is suggested that those who are interested in these processes secure at least one book on the subject involved.

Other milk by-products not discussed include such items as spray-process and roller-process dried milk, malted milk, condensed and dried buttermilk, milk sugar (lactose), whey and whey solids, and casein.

MILK OF MAGNESIA

Magnesium hydroxide, or milk of magnesia, is produced from sea water along with other magnesium compounds. Since it is used for medicinal purposes, purity of product is an important factor in its manufacture.

Production

Materials of Construction.—The large tanks used in the early stages of the process of the handling of sea water are made of steel or Douglas fir. Filters are Monel or black iron. Kettles are made of Douglas fir, Monel, or glass-lined steel. Pumps are chrome-nickel stainless steel, cast iron, or Monel. Valves are brass if air is kept out, piping is galvanized iron or brass if air is not present, and mixing equipment is nickel-clad steel or galvanized iron.

Process.—Magnesium hydroxide, oxides, and carbonates are produced from sea water by the Marine Magnesium Products Corp. at South San Francisco, Calif. (Anon., Magnesium Chemicals, *Chem. Eng.*, Vol. 54, No. 8, pp. 132–135, 1947.) Sea water is first treated at the intake with chlorine to kill the organic matter. It is next treated with a small amount of milk of lime in a mixing tank equipped with flocculating paddles. The mixture flows to a large steel settling tank in which the flocs of magnesium hydroxide holding particles of $CaCO_3$, silica, iron, and organic matter are removed from the bottoms. The clear effluent passes through a sand filter and into a large steel precipitation tank, where more milk of lime is added. Here the magnesium hydroxide concentration is increased from 0.5 per cent at the top to 12 per cent at the bottom of the tank. This slurry, containing 88 per cent sea water with 3 per cent salt, is sent through Monel plates, having 5,000 holes, at the top of two steel washing towers in series. Fresh water is introduced into the center of the washers. Concentrate from the bottom of the second tower contains 10 per cent magnesium hydroxide with 0.05 per cent salt.

Part of this concentrate goes to carbonating kettles and is treated with carbon dioxide from boiler flue gas. It is then treated with steam, vacuum filtered, and dried in a special tunnel dryer to produce dry magnesium carbonate. By elimination of carbon dioxide and water vapor, U.S.P. or rubber-grade light magnesium oxide is produced.

Another part of the 10 per cent magnesium hydroxide slurry is treated and diluted with steam and passed through a Monel vacuum filter, which increases the solids contents from 7 to 30 per cent. This paste is packaged. By injecting water into this paste and spray drying, dry $Mg(OH)_2$ powder is produced. By heating this powder to 1000 to 2000°F. U.S.P. heavy magnesium oxide is manufactured. U.S.P. milk of magnesia, containing 8 per cent water, is made by screening and diluting part of the 10 per cent magnesium hydroxide concentrates from the washing towers.

Packaging

Milk of magnesia is packaged in glass bottles or galvanized steel barrels. Rubber gaskets must not be used. Paper or unbleached hemp should be used.

MIXED ACIDS

The term "mixed acids" is used to designate mixtures of nitric and sulphuric acids. Many acid manufacturers offer mixed acids in proportions suitable for the explosives or other industries. The following formulas are typical of those on the market:

HNO_3	H_2SO_4
19	73
29	57
29	65
36	61
45	54
46	48
47	53
70	20
84.5	12

Handling

All mixed acids can be handled in plain cast iron and steel except those formulas with 70 per cent or more nitric acid. The higher formulas can be handled with stainless steel, lead, or glass-lined steel. The sulphuric acid protects the formulas with low nitric acid content, and hence they can be treated as though they were all sulphuric acid.

Type 316 stainless steel is usually more satisfactory for handling mixed acids, although Type 304 stainless is sometimes used, depending upon the ratio of the two acids, their dilution, and the temperature involved.

Hastelloy C can handle mixed acids. Worthite pumps and valves are in service. Durimet 20 offers greater resistance to mixed acids than 18-8 stainless steel.

When preparing mixed acids in a plain steel tank it is essential to run in the sulphuric acid first followed by the nitric acid.

Packaging

Plain or stainless steel is used depending upon the formula.

MONOCHLORACETIC ACID

This acid is a white flaky solid occurring in three crystal forms: α, β, and γ. It is somewhat stronger than acetic acid and is soluble in water, carbon bisulphide, and several of the common organic solvents.

Production

Materials of Construction.—Karbate is used for pumps and all other heat-transfer equipment for temperatures as high as 100°C. Otherwise, Haveg equipment is used. Karbate is used for the storage tank holding mother liquor from the centrifugal. Glass-lined chlorinators, storage tanks, and piping are used by some manufacturers. Monel pipe lines and Monel centrifugals are used for the final product when at room temperature. Saran-lined steel pipe is used at 20 to 50°C.

Process.—This acid is prepared by passing chlorine through glacial acetic acid at a temperature of 212°F., with red phosphorus as the catalyst. (Chisholm, C. G., Hastelloy, *Chem. Eng.*, Vol. 53, No. 12, p. 206, 1946.) The presence of chlorine and the catalyst require the use of a corrosive-resistant material such as Hastelloy C to ensure long equipment life.

Packaging

It is shipped in wooden barrels.

MONOCHLORBENZENE

Monochlorbenzene is used among other purposes as an intermediate for the production of synthetic phenol. It is not corrosive to ordinary materials, but one of the raw materials from which it is made is chlorine. When the chlorine and benzene are dried, no trouble is encountered.

Production

Materials of Construction.—Chlorine from the electrolytic cells is handled in chemical-stoneware pipe lines and drying tower and glass coolers. Dried chlorine is handled in ordinary cast iron. The chlorinator is ordinary steel.

The gases from the chlorinator are cooled in a shell and tube heat exchanger. Brass and Hastelloy B have been found by experience to be more satisfactory than plain steel, for the latter is more apt to foul up on the water side and thus lower the heat-transfer rate. A Karbate-tantalum absorber is used. Acid is stored either in rubber-lined steel tanks or in concrete tanks lined with brick and sulphur-base cement. For acid lines from the absorber to the storage tanks porcelain, glass, and Haveg have been found to be satisfactory. The liquid leaving the chlorinator is separated into its components in ordinary cast iron and steel.

Process.—Monochlorbenzene is made by treating benzene and chlorine in a steel chlorinator. It is not necessary to use a catalyst. Chlorine leaves the cells by means of stoneware pipe lines connected to a header. It is cooled in a glass heat exchanger. The gas is then dried in a tower by allowing sulphuric acid to come in contact with the gas in countercurrent flow. After drying, the gas passes to compressors and then to the chlorinator. Here it comes into contact with benzene dried by distillation and pumped continuously to the chlorinator. The benzene is chlorinated. Every effort is made to keep the entire system dry so as to avoid corrosion and to prevent leaks.

Gases leave the chlorinator at 180°F. and are cooled in a shell and tube heat exchanger. Cooled gases go to an absorber, where they are absorbed in water to form 32 to 33 per cent hydrochloric acid.

The liquid leaving the chlorinator is composed of unreacted benzene, monochlorbenzene, and dichlorbenzenes. It is first neutralized with caustic by contact in a centrifugal high-speed pump, then it goes to the chlorinated products steel storage tank from which the clear layer is decanted and pumped continuously to the benzene tower. Chlorbenzenes are removed from the bottom of the column and are pumped to another column, the monochlorbenzene tower. The monochlor is distilled off and goes to a storage tank; the dichlors are drained off. They may be sold as crude or separated and sold as pure products.

Refrigeration is used to separate orthodichlorbenzol from the paradichlorbenzol. The mixture is pumped to a refrigerated steel tank, where the paradichlorbenzol crystallizes. The mass is conveyed by a slurry pump to a centrifuge. From here, after the para and ortho are separated, the crystalline para is conveyed to the melter. The para is melted, cast into a pan, conveyed to a crusher, screened, and shipped. Liquid orthodichlorbenzol is pumped by steel pumps from the centrifuge to storage, put into drums, and shipped.

Handling

Pure monochlorbenzene can be handled by ordinary materials of construction without trouble from corrosion.

Packaging

Shipping is generally done in steel drums and tank cars.

MONOSODIUM GLUTAMATE

Monosodium glutamate is made from glutamic acid, which is produced by hydrolysis of natural raw materials from farm sources. The acid can be made by organic synthesis, but thus far no economical method has been developed. At present the raw materials are corn gluten, wheat gluten, soybean protein (in the Orient), and sugar beets. Both acid and alkaline hydrolysis can be used. The latter is employed to produce monosodium glutamate from beet-sugar solutions and the former for wheat gluten solutions in the process to be described here.

Production

Materials of Construction.—Regardless of the process used, monosodium glutamate corrosion problems are of great magnitude. Glass-lined equipment has proved to be excellent, as few other materials of construction will withstand the extremely severe conditions occasioned by the use of hot concentrated hydrochloric acid and at the same time avoid all contamination by metal, which would render the production of white crystals impossible. In some cases all-glass-lined digesters are used; in others the glass-lined digesters are equipped with Haveg tops. Glass-lined distillation assemblies consist of stills, columns, vacuum receivers, intermediate pipe, and fittings, including the vapor line from the still to the primary tantalum condenser. Glass-lined crystallizing pans are favored by some engineers.

Hard-rubber-covered plate-and-frame filter presses are used in some plants. Rubber-lined equipment has given poor service unless properly made. The wartime rubber compounds containing synthetic material were not satisfactory.

Some plants use tantalum bayonet heaters for (1) digesting gluten in hydrochloric acid, (2) evaporating hydrochloric acid from digested glutens so that the product will not be too salty after neutralization with caustic, and (3) condensing vapors of dilute hydrochloric acid under vacuum during evaporation just mentioned.

In several Chinese plants, in which soybean products are hydrolyzed to make food flavors, tantalum bayonet heaters and condensers are used. Much of the other equipment in these plants is Haveg construction. Inconel is used for evaporators.

All equipment used in the refining operation of some plants is made of stainless steel, including the single-effect evaporator pan. Only one type has been found even reasonably satisfactory.

Wheat Process.—In this process the raw material is the gluten milled from wheat. Briefly, the process consists of the digestion of gluten with strong hot hydrochloric acid, followed by filtration, evaporation under vacuum, crystallization of the hydrochloride of glutamic acid, then treatment with caustic soda, and crystallization of the finished product.

The digestion is carried out with strong hydrochloric acid in glass-lined, jacketed reactors. The condenser is tantalum, and outlet valves are chemical stoneware. After the digestion is complete, the solution containing a considerable amount of an insoluble sludge or organic matter is blown through a rubber-covered plate-and-frame filter press. The filtrate, now a solution of the hydrochloride of glutamic acid plus residual hydrochloric acid, is then discharged through a hard-rubber pump and pipe line into the vacuum still. In this glass-lined distillation assembly with the tantalum condenser the solution is evaporated. The outlet valves are lubricated stoneware.

The concentrated solution is discharged from the vacuum still into a series of chemical-stoneware crocks, in which, after cooling, the hydrochloride of glutamic acid separates as brownish crystals after cooling and agitation with wooden paddles.

Crystals are dissolved in water in a jacketed glass-lined tank with enameled agitator and are neutralized with caustic soda. This solution of sodium glutamate is run into glass-lined pans, where the final product separates as fine white crystals, after which it is centrifuged, dried, and packed for shipment.

Steffens Waste Process.—The Steffens filtrate from the beet-sugar refinery is first carbonated with lime-kiln gases. (Manning, P. D. V., Food Flavor from Beet Sugar By-product, *Chem. Eng.*, Vol. 55, No. 4, pp. 100–101, 136–139, 1948.) After the calcium carbonate is filtered off, the filtrate is concentrated to 65 per cent solids. It is then pumped to storage tanks.

The concentrate goes to an Oliver precoat filter, and the suspended solids are washed to the sewer. The liquid is pumped into a steel hydrolyzing tank along with 50 per cent caustic soda solution. The temperature and pH are carefully controlled. Here the pyrrolidone carboxylic acid (the internal anhydride of glutamic acid) formed from the glutamine is hydrolyzed to glutamic acid. When the acid is cooled, the hydrolysate is acidified with hydrochloric acid and concentrated. The evaporating system consists of an outside stainless-steel heater and rubber-lined flash chamber. The mineral salts are removed by a continuous centrifugal. The pH of the solution is adjusted. The solution is chilled by refrigeration in a Karbate heat exchanger and passed to a rubber-lined crystallizer. Glutamic acid crystals form along with sodium chloride and other solids. The slurry goes to rubber-lined Dorr thickeners. The underflow is passed through plate-and-frame filter presses along with the filtrate from the centrifugals. The filtrate goes to waste or by-product operations.

Crude glutamic acid from the centrifugals is then refined. The refined acid is converted into a solution of monosodium glutamate by caustic soda. It is concentrated in a stainless-steel single-effect evaporator pan. The acid is crystallized in La Feville machines. The slurry is discharged, centrifuged, and dried in a hot-air rotary-drum dryer.

Packaging

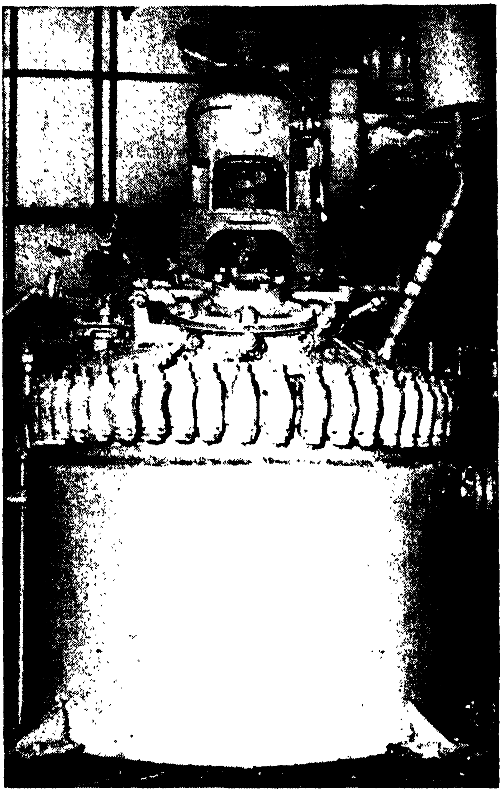
Monosodium glutamate is packed in fiber drums.

Mustard manufacture calls for chemical stoneware piping and lagged processing vessel.

NAPHTHALENE SULPHONIC ACID—FORMALDEHYDE

Corrosion tests have been made in the condensation of naphthalene sulphonic acid with formaldehyde. Monel has shown suitable resistance in this application at 230°F. However, when operating at 240 to 293°F. under 50 psi. pressure, there was evidence that sufficient sulphur dioxide might have collected in the upper part of the vessel significantly to increase corrosion in the vapor phase. A Monel agitator and shaft was used in this reactor, and the shaft showed some increased corrosion in the vapor phase. (International Nickel Co., *Tech. Bull.*, T-3.) Also refer to Alkyl Aryl Sulphonates.

Glass-lined steel reactors are in entirely successful use for this purpose at high temperatures and with no vapor-phase corrosion.



Temperatures as high as 350 to 400°F. under high vacuum conditions are reached in this chemical reactor, which is sealed by a silicone rubber gasket.

NAVAL STORES

The raw materials for the production of naval stores include those species of wood commonly classed as coniferous. Either the gum that flows from the living longleaf or slash pine or the stumps from the cutover pine forests, together with other resinous wood wastes, form the source of raw material for the various processes employed. (Shreve, R. N., "The Chemical Process Industries," 1st ed., p. 693, McGraw-Hill Book Company, Inc., New York, 1945.)

Production

Materials of Construction.—Among the metals most generally used for the processing and handling of naval stores are aluminum, copper, ordinary iron and steel, stainless steel, and wood.

Aluminum.—Equipment of aluminum is used throughout the industry for collecting, handling, and processing naval stores products. The sap from the pine trees is collected in aluminum cups, which do not contaminate the fluid and are not affected by atmospheric corrosion. Pine oil and turpentine stills, condensers, and filters and storage tanks for both crude and refined pine oil, turpentine, pinene, and dipentene are made of aluminum. (Aluminum Co. of America, "Aluminum in the Chemical Industry," p. 9.) Aluminum alloys 2S and 3S are most generally used.

Stainless Steel.—Vapors obtained in steaming wood chips to extract turpentine or to remove petroleum solvent after solvent extraction are extremely corrosive to iron or steel by reason of the acetic acid which is present and which becomes especially active at the point of condensation. Here stainless steel has been adopted with a certain amount of success. (Copper in Construction of Chemical Plants, *Chem. Age,* p. 418, May 8, 1937.)

A Newark, N.J., plant has a scale-mounted steam-heated stainless-steel rosin tank covered with mineral-wool block. Steam coils keep the temperature of the rosin at 340°F. Stainless-steel-jacketed rosin pipes leading to the tank are insulated with mineral-wool pipe covering.

Copper.—This metal has been serviceable for use in this industry for processing and handling purposes. It is used for vapor lines, condensers, turpentine stills, and other purposes.

Steel and Cast Iron.—Ordinary steel and cast iron are used to some extent. Steel extractors are in use for solvent extraction in new plants. Cast-iron pumps are also in use.

Gum Turpentine and Rosin Process.—These materials are obtained by notching the growing pine tree. (Nealy, J. B., Distilling Pine Products at New Orleans, *Chem. & Met. Eng.*, Vol. 43, No. 1, pp. 20–21, 1936.) The gum sap is collected and is distilled in a copper pot still usually situated in the pine forest. The distillate is finished turpentine. The residue is rosin. The rosin contains sand, chips, and leaves, and to clean it, it is strained while hot through cotton batting. This batting contains considerable rosin. It is placed in steel tanks with naphtha, which dissolves the rosin, and the solution is pumped out, leaving dirt and cotton behind. The naphtha is then distilled off, leaving a pure rosin.

Destructively Distilled Wood Turpentine.—Pine wood is put into retorts, horizontal steel cylinders set in a brick furnace. (*Ibid.*) Vapors and gases from the distillation go over from the retort into a condenser. The portion condensed is drained off into an open tub. Noncondensable gases are removed by the collecting header. The condensate in the tubes is pumped into settling tanks made of wood to withstand the pyroligneous liquor. The lighter and heavier oils, after treatment and filtration, are recombined and pumped into pot-type stills.

The light crudes containing turpentine, pine oil, and dipentene go over first and are condensed by water-cooled coils. The residue, pine tar, is pumped into tank cars, to the barreling warehouse, or to storage.

Condensed light crudes are agitated with sulphuric acid for bleaching and, after the acid has settled out, are again distilled, this time in a pot still with a fractionating column and in the presence of caustic. The distillate is separated and pumped to separate storage tanks. The crudes are then refined by redistilling in a pot still with a fractionating column. Rosin reclamation is a separate division of the plant.

Steam and Solvent Turpentine.—The conversion of roots, stumps, and top wood of longleaf yellow pine starts by hogging and shredding. (Hightower, J. V., From Pine Stumps to Rosin and Terpene Oils, *Chem. Eng.*, Vol. 54, No. 12, pp. 119–121, 1947.) Rubber belt conveyors move the chips and fines to storage and from there to steel extractors. The chips are supported on the bottom by a steel screen resting on a perforated plate.

Extraction with solvent takes place at 265 to 280°F. and 65 to 85 psi. gage. Spent chips are used as fuel. Leaving the extractor, the crude solution of rosin and terpene oils goes to the FF refinery and still house. Solvent is recovered in vertical-tube evaporators. Remaining solvent is removed in a flash tower kept under vacuum.

Rosin and terpene oil mixture is pumped to finishing towers, where steam strips terpene oils from rosin. Water is separated from terpene oils, and they are washed with 20 per cent caustic. Oils are then fractionated in batch stills, yielding turpentine, pine oil, and other components.

Still-molten rosin is diluted with naphtha to 50 per cent solution in mixing tanks, pumped into wash tanks, further diluted, and sprayed with water to wash down color bodies. Nigre is withdrawn from bottom of wash tanks. Rosin-naphtha solution is next pumped into the pale plant, where final color reduction is accomplished by adsorption on magnesium trisilicate packed in towers.

Pale rosin solution goes into evaporators for naphtha recovery. A final fractionator recovers terpene oil traces from the rosin. Most rosin is drummed for shipment.

Sulphate-pulp Turpentine Process.—Crude turpentine and pinene can be recovered from certain coniferous pulpwoods during the cooking period of a wood charge in digesters. (Anon., Turpentine Recovery in Paper Mills, *Heat Eng.*, pp. 22–25, February, 1947, Foster Wheeler Corp.) During the cooking operation in the digester turpentine vapor and other volatiles are given off and collect at the top of the digester.

Each turpentine-recovery unit includes a cyclone separator, a surface condenser, and a final turpentine separator known as a "decanter." The condenser is of horizontal floating-head type containing steel tubes.

The volatiles relieved from the digester enter the separator. The lighter air-vapor mixture, separated from the liquor and pulp particles, turns upward into the riser and passes out.

The air-vapor mixtures enter the condenser. The flow from the condenser, consisting of turpentine and water, is piped to the decanter, which completes the separation of crude turpentine.

Packaging

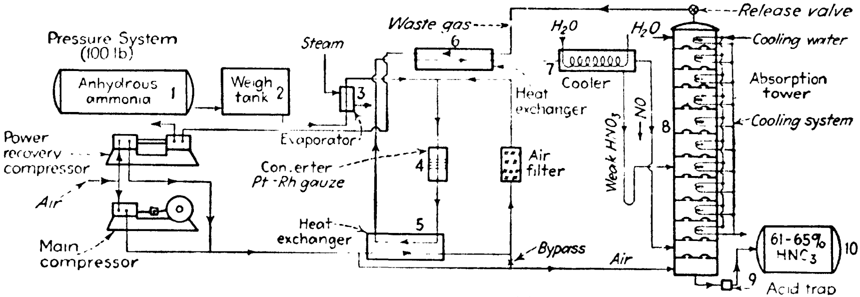
Rosin is shipped in wooden barrels or steel drums and tank cars. Turpentine can be shipped in aluminum drums.

NITRIC ACID

Nitric acid is produced by two processes: (1) ammonia oxidation and (2) from sodium nitrate and sulphuric acid, or as the latter process is sometimes known, the saltpeter process. However, the second method is almost extinct at this time in the United States.

Production

Materials of Construction.—The first synthetic nitric acid plant was constructed of the 15 to 18 per cent chromium steel Type 430 by Du Pont at Gibbstown, N.J., in 1926. Equipment in this plant was of riveted construction. Not long after this came the development of 15 to 16 per cent chromium steel containing 0.10 per cent maximum carbon. This modified Type 430 must be heat-treated. It was found that this was the range of chromium content which would give the optimum combination of chemical and physical characteristics. All other elements being equal, the corrosion resistance of the straight chromium steels to the boiling nitric acid or other strong oxidizing mediums is increased as the chromium is increased. Therefore, the adoption of a lower chromium content for the manufacture of nitric acid equipment meant sacrificing some corrosion resistance to obtain better shock resistance.



Synthetic nitric acid.

1. Steel
2. Steel
3. Steel
4. Type 347 or 430 stainless steel with aluminum fittings at top, nickel sleeve, silica bottom plate, refractory chamber, platinum-rhodium catalyst
5. Type 347 or 430 stainless-steel tubes
6. Type 304 or 430 stainless steel
7. Type 304 or 430 stainless steel
8. Type 304, 347, or 430 stainless steel, acid-proof brick or stoneware
9. High-silicon iron, Type 304, 347, 430 stainless steel, Worthite
10. Type 304, 347, 430 stainless steel, glass-lined steel, Pyroflex with fused-on ceramic lining

Gradually, welded construction began to displace riveted construction, so that by 1936 nearly all straight chromium-steel equipment was fabricated by welding. During the war, nitric acid plants were made of both welded Types 347 and 430 (15 to 16 per cent chromium steel). Also, all-welded tank cars were constructed of these materials to transport all concentrations of nitric acid.

Metallurgists have now found out how to stabilize Type 304 stainless steel with columbium, which is known as Type 347. This steel has better corrosion resistance than 430 and can be welded and stress-relieved. In wartime, plant equipment could be readily repaired without subsequent heat-treatment. Therefore most future nitric acid plants will probably be constructed of the chromium-nickel steel, Type 347.

Ammonia-oxidation Process.—Oxidation of ammonia and the absorption of the resulting oxides of nitrogen to form nitric acid are carried out in some plants at atmospheric pressure, but a pressure of 100 psi. is now more general. The equipment and the materials of construction in both atmospheric and 100-lb. pressure plants are fairly similar; therefore no distinction will be made here.

The ammonia-oxidation process is not complicated. It consists of mixing anhydrous ammonia with preheated air, passing the mixture over a platinum-rhodium catalyst, cooling, adding secondary air, and absorbing the nitric oxide in water to form the acid.

The anhydrous ammonia is stored in steel tanks. As required, it goes to a steel weigh tank and a steel evaporator, where it is evaporated continuously, steam being used to supply the heat.

It is usual to preheat the air and mix it with ammonia just before entering the catalyst chamber. Those parts of the system through which this mixture of gases pass should be fabricated of aluminum, Type 430 stainless steel, nickel, or silica in order to avoid decomposition of the ammonia.

The ammonia is oxidized with air in a Type 430 or 347 stainless-steel converter by passing it through the catalyst gauze at 1700°F. The latter type of steel is equally good or better and is often selected because of its better welding and fabricating properties. Generally when Type 430 is chosen, it is done because this type is more economical.

A typical catalyst chamber includes an aluminum fitting at the top through which the gas enters. The gas passes downward through a nickel sleeve and then through the catalyst. This consists of several layers of platinum or platinum-rhodium gauze held in a cylinder. It is closed at the bottom by a silica plate. The gauze cylinder is enclosed in a chamber of refractory material so that the heat which is liberated by the reaction can radiate to the catalyst. The catalyst chamber is enclosed in firebrick in the steel shell.

The gas (oxides of nitrogen) leaving the catalyst chamber passes through heat exchangers with tubes of Type 347 or 430 stainless steel. These preheat the air. The gas and excess air for the succeeding steps are further cooled in a water cooler and taken to the bottom of the bubble-cap absorption tower. Successive oxidations and hydrations of the nitric oxide are carried out with continuous water cooling in the tower of 304, 430, or 347 stainless steel. In very small plants these towers may be built of acidproof stoneware or brick. The absorption towers may be packed with high-silicon iron, porcelain, stoneware, or glass.

The acid is drawn off from the base of the tower through a trap of high-silicon iron; 430, 304, or 307 stainless steel; Worthite; or Durimet 20 and is handled by outflow pumps of any one of these materials. From there the acid goes to storage tanks of any one of the three stainless steels, glass-lined steel, or Pyroflex with fused-on ceramic lining. In one plant 43 per cent acid is stored in concrete tanks lined with acidproof brick.

Saltpeter Process.—Sodium nitrate is dried in a rotary dryer and is charged together with sulphuric acid into a warm retort. Partly dissociated nitric acid vapor is distilled into a condenser. The acid passes to a cooler and is drawn off. The weak acid generally contains lower oxides of nitrogen and is passed through a bleacher, where they are removed by a current of air. The products of dissociation which pass the condenser go to a series of towers where they are absorbed in water. The result is to produce additional weak acid which is added to the weak acid from the condenser. At the end of the system of absorbing towers some device is used to carry this part of the system under slight vacuum. The gaseous products leaving the absorbing towers are simply discharged into the air. The water in the absorbing towers is circulated over each tower a number of times, and the air now introduced assists in the oxidation and recovery of the lower oxides of nitrogen. (Badger, W. L., and E. M. Baker, "Inorganic Chemical Technology," 2d ed., p. 81, McGraw-Hill Book Company, Inc., New York, 1941.)

The equipment includes a retort mounted in a brick structure. The retort can be cast iron, high-silicon iron, 18 per cent chrome iron, or 18-8 chrome-nickel steel. The acid sodium sulphate, or niter cake, withdrawn from the retort is acid and therefore difficult to handle. It is generally run onto floors of acidproof brick to solidify or chilled by a stainless-steel flaking roll.

Nitric acid vapor from retorts is handled through high-silicon lines and is cooled and condensed in S bends of fused silica, high-silicon iron, stoneware, glass, or stainless steel. Recombination of the oxides of nitrogen takes place in absorption towers made of acidproof brick, stoneware, high-silicon iron, or stainless steel. The packing can be quartz, acidproof brick, or stoneware.

Concentration.—The weak nitric acid can be concentrated to 95 to 99 per cent, the strengths generally used for fortifying acids for nitrations and other purposes. To obtain these concentrations it is now customary to dehydrate the nitric acid with strong sulphuric acid. High-silicon iron concentrators are widely used. In some of the other plants direct-fired pot stills were used. More recently these have been replaced by the Pauling, Hechenbleikner, Davis *et al.*, Peterson *et al.*, and Zeisberg concentrators.

In a plant using the Zeisberg system for concentration the weak nitric is pumped to a mixing tank where the sulphuric acid is added. From there the mixed acid is pumped to the high-silicon iron dehydrating tower through high-silicon iron pipe. The 99 per cent nitric acid vapors leaving the top of the dehydrating tower go through high-silicon iron condenser coils to storage tanks. These tanks are Type 347 stainless steel. Nitric above 95 per cent can be stored either in straight chromium, Type 430, or chromium-nickel types of stainless steel or in aluminum.

Passing off from the bottom of the dehydrating tower is sulphuric acid containing 7 per cent nitric acid. This mixed acid goes to the denitrating tower. It is made of steel-lead-brick construction. The distribution plate at the top and steam distribution at the bottom are high-silicon iron. In this latter tower the remaining nitric acid is separated and returned through high-silicon iron vapor lines to the dehydrating tower. The sulphuric acid after being stripped of nitric acid, which is boiling and at a concentration of 66 to 68 per cent, goes through lead or high-silicon iron lines to cooling coils of high-silicon iron, Karbate, Hastelloy, or lead. Here it is cooled to atmospheric temperature and goes to steel storage tanks. (Anon., *Chem. & Met. Eng.*, Vol. 52, No. 8, p. 177, 1945.)

Treatment with Oxygen.—The treatment of a mixture of dilute nitric acid and nitrogen tetroxide by oxygen under high pressure is used. The oxygen is forced into the mixing chamber beneath the converter, where it is mixed with ammonia gas. The oxygen and ammonia mixture then has steam added to it. The mixture is then burned on the platinum or platinum-rhodium gauzes. Products of combustion pass upward through a waste heat boiler. From the boiler the gases pass to a condensate catcher, where the steam and part of the water formed during the combustion are condensed out. The gases consisting of nitric oxide, nitrogen peroxide, oxygen, and water vapor are cooled, and the nitric oxide partially oxidized to nitrogen peroxide in the gas cooler, from which the condensate consisting of nitric acid of 50 per cent is obtained and transferred to the raw mixture tank.

Oxidation of the nitric oxide is completed in the oxidation tower. The gases pass to an aftercooler, where nitric acid of 70 per cent is condensed out and transferred to the mixing tower. Gases from the aftercooler contain pure nitrogen tetroxide, which is condensed in a brine-cooled liquefier, from which it flows to the mixing vessel. Residual gases from the liquefier pass to an aftercooler, which is provided with a brine-cooled jacket, where they are scrubbed with cooled 98 per cent nitric acid. Acid from the absorber is transferred to an overhead tank for subsequent degasification. Those parts of the condensate catcher, gas cooler, oxidation tower, aftercooler, and interconnecting mains which are in contact with the nitrous gases and nitric acid are constructed of acid-resisting steel. The NO_2 liquefier is made of aluminum. (Manning, A. H., Production of Concentrated Nitric Acid, *Trans. I.C.E.*, Vol. 20, p. 97, 1942.)

Handling

Stainless Steels.—Grades in both the 400 series (straight chromium) and the 300 series (chromium-nickel) containing a minimum of 16 per cent chromium are very resistant to all concentrations of nitric acid at temperatures used in the ammonia-oxidation process. All these grades are highly resistant to all concentrations up to 70 per cent at temperatures up to or slightly below the boiling point. Higher concentrations, particularly 90 to 99 per cent, will corrode stainless steel rapidly at temperatures above 125°F. At these higher concentrations stainless steel is mainly used for handling the acids at atmospheric temperatures. The successful development of the ammonia-oxidation process was based upon the corrosion resistance of stainless steel, which is used almost entirely throughout the system involving absorption towers, heat exchangers, piping, valves and pumps, etc. Similar equipment is practically indispensable in the production of dyestuffs, high-power explosives, and artificial silk and in the numerous other industries which depend wholly or in part on the satisfactory handling of acid.

Where nitric acid solutions of any concentration are involved at room temperature, all the stainless-steel grades exhibit satisfactory corrosion resistance, and selection of material is determined by physical requirements. The better ductility or weldability of the chromium-nickel grades is often desirable. As the service conditions become more severe with increasing temperature or concentration, the high-chromium-nickel grades may be superior to the lower alloy grades, such as Type 410, containing only 12 per cent chromium. The straight chromium grades containing at least 17 per cent chromium and all the chromium-nickel grades are highly resistant to 50 per cent nitric acid at the boiling temperature.

Molybdenum additions, as found in Types 316 and 317, do not improve the resistance to nitric acid corrosion. In some instances, Types 316 and 317 are less resistant than the regular 18-8 grades. Types 309 and 310 are especially well suited for service at high temperatures and pressures, and these grades can be used with or without columbium.

The standard nitric acid corrosion test, which is well known and accepted as one of the most dependable methods for laboratory testing and evaluating the corrosion resistance of stainless steel, provides a good indication of the performance that can be expected under severe operating conditions. Average typical corrosion rates for the various superior grades immersed in boiling 65 per cent chemically pure nitric acid solution (sp. gr. 1,398) for five periods of 48 hr. each are shown below. New acid is used for each period of the test.

Type	*Corrosion Rate, Mils per Year*
430	Less than 60
304	Less than 12
347	9.6–14.4
308	Less than 12
309	Less than 12
309 Cb	4.8–8.4
310	Less than 12

The unmodified chromium-nickel steels which contain precipitated carbides resulting from heating too long in the 800 to 1500°F. temperature range are subject to intergranular corrosion in the presence of nitric acid. Types 347, 309 Cb, and 310 Cb contain columbium additions which prevent harmful carbide precipitation. These grades must be used if heavy welded sections are required or if large units are stress-relieved after fabrication. Type 347 is satisfactory for temperatures below the boiling point, while Types 309 Cb and 310 Cb are better suited for temperatures above the boiling point.

Considerable attention recently has been given to stainless-steel chambers for fuming nitric acid used in rockets. Laboratory tests have shown that stainless steel offers good resistance to fuming nitric acid liquid and vapors at room temperature. This is one of the most severe intergranular corrosion agents known.

Field experience does not always correspond with the results of laboratory tests, probably because high pressures and stresses which cannot be duplicated in the laboratory are often involved in service conditions in the field. (Snair, G. L., Jr., Stainless Steel, *Chem. Eng.*, Vol. 55, No. 3, p. 228, 1948.)

High-silicon Iron.—Nitric acid and many solutions containing nitric acid have been successfully handled by the high-silicon irons for a number of decades. The excellent resistance of high-silicon iron to the strong, active acids such as nitric and sulphuric has long been recognized by corrosion engineers. Its susceptibility to thermal and mechanical shock, however, has somewhat limited its use, but abnormally high temperatures are constantly being handled when proper care is exercised. This alloy is also relatively inexpensive compared with other corrosion-resistant materials employed for acid services. It is supplied in the cast form only and owing to its extreme hardness can be machined only by grinding methods. The high-silicon content results in an alloy with low tensile strength and high compression strength; therefore the design of equipment keeps stresses in compression whenever possible.

High-silicon iron is unattacked by all concentrations of nitric acid at normal temperatures. Increasing the temperature has very little effect on its corrosion resistance. Boiling nitric acid at concentrations above 50 per cent has no effect on high-silicon iron, although weak solutions do show a very slight attack. Hot concentrated nitric acid, which rapidly corrodes stainless steels, has practically no effect on high-silicon iron. For this reason high-silicon iron pumps, valves, piping, condensers, fans, and tower sections are extensively used in the production of nitric acid and also in handling the acid in other processes.

The resistance of high-silicon iron to nitric acid solutions containing other constituents depends entirely on its resistance to these other constituents. (Luce, W. A., High-Silicon Iron, *Chem. Eng.*, Vol. 55, No. 3, p. 225, 1948.)

One chemical engineer in an acid plant reports that high-silicon iron pipe, tanks, pots, and plug cocks have been used in many places and have not given any evidence of corrosion. However, plug valves of this material are unsatisfactory because they are easily broken in opening and closing by operators. They are being replaced by stainless-steel valves.

Worthite.—Experience, as well as laboratory investigation, has demonstrated that Worthite is an unusually satisfactory material for pumps and valves for the transfer of all concentrations and temperatures of nitric acid. This holds true not only in the manufacture of nitric acid but also in the production of dyes, explosives, and other nitration processes.

A Southern nitric acid plant reports having 35 Worthite pumps in use circulating acid at the towers. These pumps have been in continuous use for 7 years with very little evidence of corrosion.

Generally speaking, all stainless steels of iron and 13 per cent or more chromium are resistant to oxidizing mediums, such as nitric acid. Worthite is of the stainless class but exceeds the standard types in alloy content.

The first installation of Worthite pumps in the manufacture of nitric acid was at a large Western ordnance works. Here 21 were used with 60 lb. pressure.

Using water seals of 80 lb. pressure, nitric acid was handled satisfactorily at all strengths as its concentration was increased from tower to tower, seven towers per unit. In view of the experience obtained from this installation potential trouble with this process can be avoided by specifying pumps with solid shaft construction, eliminating the necessity for a shaft sleeve. Generally speaking, it has been found that with high-pressure services trouble can develop when tight packing shuts off the water seal and causes expansion of the shaft sleeve by overheating. This can result in a loosened impeller, scored suction head, and sometimes even a shaft breakage. (Collinsworth, E. T., Jr., Worthite, *Chem. Eng.*, Vol. 55, No. 4, p. 219, 1948.)

Carbon.—Nongraphitic (amorphous) carbon is generally preferred for nitric acid conditions where heat transfer is not a problem. Its most widespread use is in mixtures of nitric acid with other highly corrosive materials of a nonoxidizing character.

Where heat transfer is involved, Karbate impervious graphite is used successfully. While slow progressive attack may be expected on the impregnating resins used to fill the natural pores, life of several years has been obtained on this equipment operating in solutions containing 10 and 40 per cent HNO_3 at 185 and 140°F., respectively. (Gaylord, W. M., Carbon and Graphite, *Chem. Eng.*, Vol. 55, No. 3, p. 225, 1948.)

Chlorimet 3.—This nickel-base alloy's high chromium content makes it applicable for most nitric acid services, but its use is generally limited because of its higher price. Conditions involving severe services with nitric acid as a minor constituent can be handled with this alloy. (Luce, W. A., Durimet and Chlorimet, *Chem. Eng.*, Vol. 55, No. 2, p. 233, 1948.)

Aluminum.—Most of the large producers of nitric acid, made by the ammonia-oxidation process, have for many years recognized the value of aluminum and used it extensively. Aluminum chemical equipment has given long and uninterrupted service, not only in the production of nitric acid, but also in the production of sundry products in whose manufacture nitric acid is employed.

Concentrated nitric acid (80 per cent or above) and its vapor have only slight effect on aluminum at room temperature. Since solutions of the lesser oxides of nitrogen and the gases themselves attack aluminum only superficially, it is used commercially in reaction vessels for the catalytic oxidation of NH_3, and cooling coils or condensers for the concentration of the acid, as well as pressure piping. To handle concentrated nitric acid (80 per cent or greater) made by the ammonia-oxidation process, aluminum-alloy storage tanks, I.C.C.-approved tank cars, siphons, and containers are employed.

Nitrous gases can as a rule be handled in aluminum, although the lower oxides, when dissolved in nitric acid, may increase the rate of attack slightly. Aluminum hoods, ducts, and covers for nitrating tanks are widely used for the handling of gases which contain oxides of nitrogen.

In the manufacture of nitric acid-base explosives, the nonsparking property of aluminum, as well as its corrosion resistance, is used to advantage. Aluminum evaporators and crystallizers have been used for the processing of ammonium nitrate, thereby avoiding harmful contamination. (Balash, J. P., and E. D. Verink, Jr., Aluminum, *Chem. Eng.*, Vol. 55, No. 2, p. 236, 1948.)

Durimet 20.—It gives excellent resistance to nitric acid at all concentrations and temperatures. The highly oxidizing character of this acid is ideal for Durimet 20, which normally depends on the formation of a "passive" film for its corrosion resistance.

High-silicon iron is generally preferred over Durimet 20 in nitric acid service when cost is paramount. However, many applications require the use of machinable alloys, and it is generally for these conditions that Durimet 20 is used. (Luce, *loc. cit.*)

Durimet 20 pumps, valves, pipe, etc., are widely used to handle nitric acid in many installations. In fact one company found the alloy to be superior to conventional low-carbon 18-8 stainless steel on hot, 97 per cent acid.

Hastelloy C.—This alloy is resistant to dilute nitric acid at temperatures up to 150°F. For nitric acid solutions of over 40 per cent concentration, this alloy is recommended for use only at room temperatures. Alloy C is the only one of the Hastelloys that possesses good oxidation resistance. But it is not generally used for straight nitric acid service because stainless steel is satisfactory for such service and is less expensive. Alloy C has been used successfully, however, with nitric acid in combination with reducing conditions that tend to remove the passivating film from the stainless steels. (Chisholm, C. G., Hastelloy, *Chem. Eng.*, Vol. 55, No. 2, p. 233, 1948.)

Stellite.—The cobalt-base alloys, particularly Stellite alloy No. 1, possess excellent resistance to nitric acid. Therefore, they can be satisfactorily used for facings on valve seats and parts subjected to nitric acid corrosion as well as to severe abrasion. (*Ibid.*)

Iron and Steel.—Nitric acid solutions up to 75 per cent by volume corrode iron or steel quite rapidly, hence the use of these metals in this service is not recommended. Concentrated nitric acid, *i.e.*, 95 per cent by volume, is much less corrosive, and iron or steel is occasionally used. (Spitz, A. W., Iron and Steel, *Chem. Eng.*, Vol. 55, No. 2, p. 233, 1948.)

Rubber Linings.—Concentrations up to 5 per cent can be handled at room temperature by semihard and flexible ebonite stocks. Concentrations up to 10 per cent at room temperature can be handled by specially compounded ebonite compounds.

A concentration of 35 per cent at temperatures up to 140°F. can be handled with soft butyl compounds. Further testing of butyl in nitric is under way. (True, O. S., Rubber Linings, *Chem. Eng.*, Vol. 55, No. 2, p. 233, 1948.)

Vinylite Lining.—Concentrated nitric acid at room temperature can be satisfactorily handled with a Vinylite lining.

Nickel and Nickel Alloys.—Monel, nickel, and Ni-Resist alloys are subject to severe attack by nitric acid and generally are not used with this acid except in extremely dilute solutions.

Inconel, because of its chromium content, is more resistant to nitric acid than any of the above materials. It is particularly resistant to nitric acid concentrations higher than about 20 per cent and below about 3 per cent at atmospheric temperature. Ordinarily it would not be used at elevated temperatures except in the dilute solutions formed by hydrolysis of some acid nitrate salts. (Friend, W. Z., Nickel, Nickel Alloys, *Chem. Eng.*, Vol. 55, No. 4, p. 219, 1948.)

Silver.—Silver is rapidly attacked by nitric acid both hot and cold. It is therefore unsuitable as a material of construction if exposed to nitric acid.

Gold.—In contrast to silver, gold is known for its resistance against nitric acid; for instance, the old art of differentiating between gold-rich alloys and those of low gold content is based on the high resistance of gold to nitric acid. Dilute nitric acid has no effect on gold; boiling nitric acid of a sp. gr. 1.5 dissolves gold only at the rate of approximately 0.185 mil per year. A substantial weight loss, however, is observed on exposing gold to boiling concentrated acid of a specific gravity of 1.42, the loss averaging 6 mils per year.

Platinum.—There is no doubt that platinum is more resistant to nitric acid even than gold. No matter what the dilution, platinum will resist the attack of nitric acid in the whole temperature range between room temperature and boiling. Even under the extreme temperature conditions of the ammonia-oxidation process (around 900°C.) platinum and its alloys show a truly excellent resistivity as catalysts. Platinum-rhodium gauze will produce in excess of 50 tons of acid per ounce of metal before it requires reworking. The metal costs only a few thousandths of a cent per pound of acid. Platinum alloys like iridium-platinum and rhodium-platinum are just as corrosion resistant as platinum itself. (Rosenblatt, E. F., Precious Metals, *Chem. Eng.*, Vol. 55, No. 2, p. 238, 1948.)

Glass-lined Steel.—This material is frequently employed for nitrations and storage, as it is inert toward nitric acid.

Protective Coatings.—Nitric acid attacks most organic materials. Concentrated nitric acid is a strongly oxidizing acid, and not until recent years have there been found nitric-resistant organic materials for regular use as film-forming agents. The following are resistant to nitric acid: polyvinyl chloride, the cojoint polymer of polyvinyl chloride, polyvinyl acetate, polyvinyledene chloride, polystyrene, methyl methacrylate, and silicone rubber.

The phenolics, ureas, melamines, cellulosics, acetates, butyrates, etc., can be used only in relatively dilute solutions or where occasional spills of weak acid are anticipated. (Anon., Protective Coatings, *Chem. Eng.*, Vol. 55, No. 4, p. 220, 1948.)

An engineer with many years' experience in nitric acid production writes that Amercoat No. 44 is the best paint he has found for contact with 43 per cent acid at 120°F. An excellent concrete paint in a nitric acid atmosphere is Corrosite. The paint 3M(EC-817) Gray Pigment has held up well after being exposed to the atmosphere in the nitric acid plant for over a year.

Gasket Materials.—Obtaining suitable gasket materials was one of the major problems at the time the chemical plants at Oak Ridge were placed in operation. The use of ordinary materials such as blue African asbestos, rubber, compounded asbestos, and metal for gaskets was totally unsatisfactory for many applications where corrosion conditions were unusual. For use with glass-lined equipment and

Pyrex-glass pipe, the gasket material must not only resist attack from the fluid being handled but also be sufficiently elastic to make tight joints possible without setting up strains in the piping or equipment. The most satisfactory material found for this service has been Tygon of medium hardness. This material will satisfactorily withstand attack of most mineral acids and oxidizing agents up to a temperature of 160°F. The material would be even more useful if it could be compounded with fine glass cloth, which would provide added strength and tend to prevent creep under pressure.

For use with metal pipe (including glass-lined) and equipment, Teflon (polytetrafluoroethylene) has been found to be the most satisfactory gasket material. This material will withstand aqueous solutions of mineral acids and oxidizing agents in all concentrations as well as a wide variety of organic compounds. Its upper temperature limit for use as a gasket material is 300°C. Because of their hardness, Teflon gaskets are used chiefly with metal joints. Even though its initial cost is relatively high, the over-all cost is not prohibitive, since Teflon gaskets can be reused a number of times. In special instances Teflon has been used satisfactorily in porcelain and Pyrex-glass pipe lines, although its use here is restricted because of the extreme care with which the piping must be aligned in order to obtain a tight but strain-free installation. Boiling the Teflon in water for 30 min. just prior to its use in porcelain or glass pipe lines has been found to aid materially in obtaining tight joints with lower flange pressures. (Schrader, R. J., and A. De Haan, Special Materials Solved Corrosion Problem at Oak Ridge, *Chem. Eng.*, Vol. 53, No. 11, p. 96, 1946.)

Illium is used extensively for pumps handling nitric acid. The alloy is used to some extent in almost every conceivable design of pump. It is used in these pumps for the impellers, bearings, journals, wearing rings, etc.

Packaging

To find out what are the most suitable materials from which to make shipping and storage drums to contain nitric acid the Manufacturing Chemists Association, through its Metal Packages Committee, sponsored a cooperative testing program. Test findings have been summarized in a report dated Oct. 23, 1947.

For drums and storage containers to contain 93 and 95 per cent nitric acid, all grades of stainless steel and aluminum tested can be used as construction materials. The six grades of steel tested were (1) Cr, 26; (2) Cr, 17; (3) Cr, 19; Ni, 9 (the 18-8 stainless); (4) Cr, 19; Ni, 11; Cb, 1 (the columbium-bearing grade); (5) Cr, 25; Ni, 14; and (6) Cr, 25; Ni, 18. The two grades of aluminum tested were the 99.6 Al and the 3S. The stainless steel must be properly heat-treated, or else it must contain the stabilizing agent columbium, as the austenitic Cr-Ni grades do, to maintain maximum corrosion resistance. Heat-treatment is not essential for aluminum. Both aluminum and stainless steel appear to have equal corrosion resistance in these concentrations of acid.

For drums or storage containers handling 97 and 99 per cent nitric acid, the following construction materials can be used: properly heat-treated 18-8 stainless steel (Type 304); columbium-bearing Type 347 stainless, not heat-treated; and aluminum grades 99.6 and 2S. For stainless steel, heat-treatment after fabrication is required unless the stabilized grade containing columbium is used. The corrosion resistance of aluminum in these concentrations of acid is much superior to that of Types 304 and 347 stainless steel. Drums made from these grades of stainless steel are entirely safe for transportation and storage of 97 and 99 per cent nitric acid, but their utility will depend upon the severity of storage conditions and the quality of acid required. Since various sources report successful use of Types 304 and 347 stainless steel for drums to contain 97 to 101 per cent nitric acid, it would appear that the conditions of the M.C.A. cooperative testing program were much more severe than those encountered in actual practice. Nitric acid also is shipped in glass bottles and carboys.

NITRIC ACID—ACETIC ACID

High-alloy stainless steels, such as Durimet 20 and Worthite equipment, are being used with a mixture of 70 per cent nitric acid and 30 per cent acetic acid and also with a solution containing from 1 to 2 per cent nitric acid and 1.2 per cent acetic acid.

Glass-lined steel is fully resistant.

NITRIC ACID—HYDROCHLORIC ACID

The combination of nitric acid and hydrochloric acid is about as corrosive a solution as it is possible to find.

Handling

Glass-lined Steel.—Some engineers (Schrader, R. J., and A. De Haan, Special Materials Solved Corrosion Problems at Oak Ridge, *Chem. Eng.*, Vol. 53, No. 11, pp. 96–101, 1946) have found glass-lined equipment to be the most satisfactory material for holding hot solutions containing high concentrations of both nitric and hydrochloric acids in large volume.

Porcelain.—This pipe has been used extensively in places where solutions containing high concentrations of both nitric and hydrochloric acids are handled. Porcelain pipe, although it can be field fabricated, is not so versatile as glass pipe in this respect. Its mechanical strength is somewhat greater, and it does not have to be protected so well. For use at Oak Ridge, however, it has few advantages over glass pipe and several major disadvantages, such as its nontransparency, lower resistance to heat shock, and greater weight, which makes supporting it more difficult. For the most part horizontal runs of porcelain pipe are supported in plywood or metal angles rather than with standard pipe hangers.

Tantalum.—One step in the chemical process at Oak Ridge involves the evaporation of a considerable volume of solution containing as high as 30 per cent nitric acid and up to 5 per cent hydrochloric acid. The only suitable material of construction found for evaporators under these conditions was tantalum, which is virtually unattacked by any mixture of these two acids. These evaporators are constructed with liners of tantalum, 0.013 in. thick, backed by heavy steel sheets. Although the tensile strength of tantalum sheet is high, its shear strength is much less, so that considerable care must be exercised in the mechanical removal of scale from the evaporator parts. Chemical cleaning procedures are used for this operation whenever possible.

For the severe attack of combined nitric and hydrochloric acid fumes, hoods are constructed of Alberene or stainless steel.

Stainless Steel.—Mixtures of nitric and hydrochloric acids are corrosive to all the stainless steels, the extent of attack depending upon the acid concentrations and the solution temperatures. (Snair, G. L., Jr., Stainless Steel, *Chem. Eng.*, Vol. 55, No. 3, p. 228, 1948.)

Hastelloy.—In cold solutions of nitric acid containing varying amounts of hydrochloric acid, Hastelloy C has shown good resistance. (Chisholm, C. G., Hastelloy, *Chem. Eng.*, Vol. 55, No. 2, p. 233, 1948.)

Graphite.—Condensers of graphite have been used with a mixture of nitric acid (estimated 10 per cent) and hydrochloric acid. Because there is no suitable cement available to withstand this extremely corrosive and oxidizing mixture, packed-tube construction was used. (Ford, C. E., Graphite Heat Exchangers, *Chem. Eng.*, Vol. 54, No. 1, pp. 92–96, 1947.)

Saran.—Saran-lined steel pipe is in service with this mixture of acids.

NITRIC ACID—HYDROFLUORIC ACID

Mixtures of nitric and hydrofluoric acids are among the most corrosive of all solutions. Mixtures of the two acids are corrosive to all the stainless steels, the extent of the attack depending upon the acid concentrations and the solution temperature. (Snair, G. L., Jr., Stainless Steels, *Chem. Eng.*, Vol. 55, No. 3, p. 228, 1948.)

The resistance of high-silicon iron to nitric acid solutions containing other constituents depends entirely on its resistance to these other constituents. Therefore, nitric acid solutions containing hydrofluoric acid, for which high-silicon iron is not recommended, may cause excessive corrosion. (Luce, W. A., High-Silicon Iron, *Chem. Eng.*, Vol. 55, No. 3, p. 225, 1948.)

In cold solutions of nitric acid containing varying amounts of hydrofluoric acid, Hastelloy C has shown good resistance. Mixtures of the two acids used for cleaning stainless steel have no effect on Koroseal.

Carbon bricks are accepted as standard construction for tank linings in the pickling of stainless steel in solutions generally ranging from 10 to 14 per cent nitric acid with 2 to 4 per cent hydrofluoric acid. Such linings have been in service for 14 years with no apparent evidence of brick deterioration. (Gaylord, W. M., Carbon and Graphite, *Chem. Eng.*, Vol. 55, No. 3, p. 225, 1948.)

Durimet steam jets are used in a steel mill in the electrolytic pickling of stainless-steel strip. The corrosive solution used is 20 per cent nitric plus 3 to 5 per cent hydrofluoric acid. (Luce, W. A., Durimet and Chlorimet, *Chem. Eng.*, Vol. 55, No. 2, p. 233, 1948.)

Stainless-steel pickle solutions contain nitric acid up to 20 per cent concentration and hydrofluoric acid up to 5 per cent at a maximum operating temperature of 160°F. This is an extremely corrosive mixture and rapidly corrodes most materials of construction. However, Durimet 20 pumps, valves, steam jets, etc., are being used extensively for this service, since they provide superior resistance to most other alloys economically practicable. This fact has been ascertained on numerous occasions by comparative plant testing. The corrosion experienced on Durimet 20 is substantial; nevertheless it is the best alloy available.

NITRIC ACID—SULPHUROUS ACID

The resistance of high-silicon irons to nitric acid solutions containing other constituents depends entirely on its resistance to these other constituents. Therefore, nitric acid solutions containing sulphurous acid, for which high-silicon iron is not recommended, may cause excessive corrosion. (Luce, W. A., High-Silicon Iron, *Chem. Eng.*, Vol. 55, No. 3, p. 225, 1948.)

NITROCELLULOSE

Nitrocellulose, or cellulose nitrate as it is sometimes known, is used for several purposes such as an explosive, in lacquers, and as a plastic.

Production

Materials of Construction.—In the nitrating area, the use of chrome-nickel steels has become more and more general. (Thoenges, E. F., Nitrocellulose, *Chem. & Met. Eng.*, Vol. 41, No. 10, p. 526, 1934.) Nitrating pots are now being made of rolled 18-8 stainless steel throughout. The use of various chrome steels in centrifugal wringers has been given considerable study by all the leading nitrocellulose manufacturers. Those parts of the centrifugal in which corrosion resistance is of chief importance, are now generally made of some chrome-nickel alloy; in those portions of the centrifugal in which safety is the governing characteristic, the introduction of chrome-nickel alloys is still in the development stage.

For fume lines to carry off acid vapors and for flume lines to carry off acid water, salt-glaze terra cotta has been standard for decades. At points where special line shapes are needed, thin chrome-iron sheet is used. Mixed-acid tank vents have proved most satisfactory when made of aluminum.

The treating tubs used for the purification of nitrocotton have been made of cypress for many years. The durability of this wood for this service is such that it has never been found practicable to replace it. To prevent contamination of the nitrocotton, the tubs are usually lined with a thin sheet of a chrome alloy of the straight 18 per cent chrome type. Tub castings are extremely satisfactory when made of a chrome alloy of the straight 26 per cent chrome type. For the tubing of the Milliken digester, in which the viscosity of the nitrocellulose is continuously reduced under conditions of elevated temperature and pressure and mild acidity, chrome-alloy tubes of the straight 18 per cent type are proving to be the proper material.

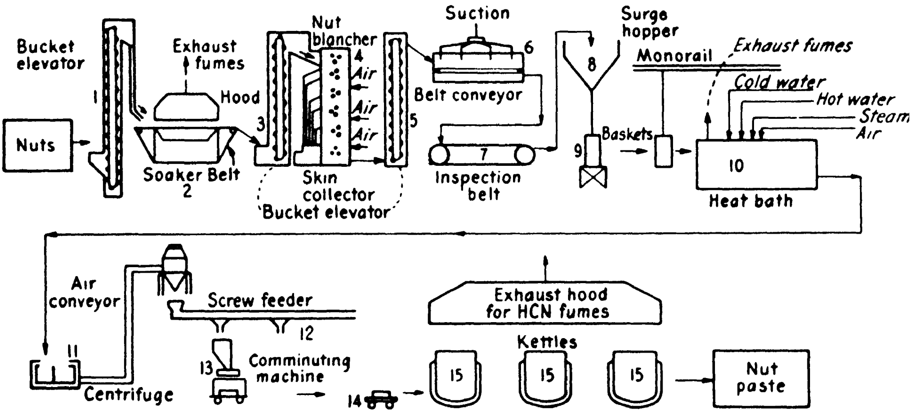
Buildings in this industry generally have a steel framework with a brick sheathing. Roofs of shortleaf yellow pine and felt roofing paper have proved to be the most practical and economical type. The most recent advance in material for construction in the industry has been the protection of steelwork generally with Parlon paints. Parlon is a chlorinated rubber compound. When properly formulated, it has proved to be the best coating for acid conditions.

Packaging

Nitrocellulose solutions are put into galvanized drums and tin-lined steel drums, also galvanized cans.

NUT PASTES

Advanced equipment and methods have both improved the quality of nut and pit pastes and speeded operations in their manufacture. (Anon., Quality Nut Pastes by Modern Means, *Food Ind.*, Vol. 20, No. 9, pp. 1278–1280, 1948.) The industry is nearing the goal of making the entire process continuous, with many steps already on that basis. Remaining batch operations are so timed that the present production is a constant flow.



Nut Paste.

1. Steel
2. Stainless steel
3. Steel
4. Steel
5. Steel
6. Steel
7. Stainless steel
8. Steel
9. Steel
10. Steel
11. Steel
12. Stainless steel
13. Stainless steel
14. Aluminum
15. Copper

Production

Materials of Construction.—In the modern plant of the National Almond Products Co., Brooklyn, N.Y., much of the equipment is steel, but some stainless steel and aluminum are used.

Process.—Three pastes—almond, kernel, and macaroon—are made, respectively, from almond nut meats, apricot pits, and a combination of the two, all with a medium and added moisture.

First, nuts are dumped into a continuous bucket elevator feeding a hot-bath soaker equipped with a continuous stainless-steel mesh belt, where skins are softened. For removal of skins, nuts then travel to an air-blast blancher and next are conveyed in a suction-line-equipped trough. The nuts finally fall on stainless-steel inspection belts.

Prussic acid, occurring in the nuts and pits, is partially removed by the washes. After the nuts are dried in high-speed basket-type centrifugals, comminuting machines grind them into bits. The bits drop into aluminum trays for delivery to the mixing kettles. The kettles remove the remaining prussic acid fumes and reduce the bits to a paste of 11 per cent moisture content. Pastes are packed direct from kettles and transferred to air-conditioned storage.

OLEOMARGARINE

Chemical engineering has played an important part in bringing the manufacture of margarine and edible fats generally to the present state of efficiency. From being a fairly perishable foodstuff in the early days, the product is now a food which can be kept in good condition for a number of weeks, even without the aid of chemical preservatives, and in reaching that position the improvements in plant have contributed greatly. (Anderson, A. J., Manufacturing of Margarine, *Trans. I.C.E.*, Vol. 22, p. 1, 1944.)

Production

Materials of Construction.—Originally, much of the plant was constructed of wood. In many respects wood, even hardwood, is an unsatisfactory material owing to its porous nature, and even with very thorough cleaning it is always liable to be a breeding ground for undesirable microorganisms. It has, however, the advantage that when wet the margarine does not adhere or stick to it as frequently occurs with metal, and hardwoods such as teak, oak, elm, and beech have been used as extensively. However, the cleaning problem was always a difficult one, and the gradual development of sponginess on the surface made frequent replacement essential. These drawbacks of wood were realized early, and attempts were made to extend the use of metal wherever possible.

Tinned steel and tinned copper, as in dairies, were the first to be employed; the presence of salt to the extent of 15 per cent or more in the aqueous phase and acidic products, such as lactic acid with a pH value as low as 4 or 5 in the serum, made the employment of plain metal useless. When it was found that some metals, particularly iron and copper, were oxidation promoters and that certain types of deterioration in fat were due to oxidation, the importance of keeping the tin coating of the iron and copper surfaces in perfect condition was further emphasized. At the same time, attempts were made to find homogeneous uncoated metals which were inert toward the margarine. Of the many which have been tried aluminum, Monel, stainless steel, and, for some purposes, nickel have established themselves and are now to be found in modern margarine factories where they are steadily replacing wood.

It is necessary not only that there should be no action between the material of construction and the margarine but also that the material should be resistant to the various chemicals and detergents necessary for cleaning and washing the plant. This cleaning is a very important part of successfully running a margarine factory, as the product, though made from sterile fats and bacteriologically controlled milk, is exposed in its passage through the works to the risk of infection from plant and the air, and even in closed plant the risk of infection is difficult to avoid altogether. A material which might be satisfactory in contact with margarine may not stand up to the cleaning operations and must therefore be avoided; for instance, certain lacquers might be satisfactory for some item of plant but for the fact that they would disintegrate during the cleaning-down process.

Tanks and ripening vats for milk and tanks for melting fats are therefore made of tinned steel, aluminum, stainless steel, and glass-lined steel. Copper is avoided as far as possible, and where used, it must be extra heavily tinned and kept well tinned. Churns and emulsifiers are made from tinned steel or stainless steel. At present, cooling drums are generally made of steel. But it would be an improvement if stainless-steel or nickel coating could be used. This is because the presence sometimes of salt in the emulsion, as well as lactic acid, and the low temperature of the surface, which leads to condensation of moisture when the drum is not in use, make it essential to take special steps to protect the steel surface against corrosion by keeping it well oiled. Wood is still used a good deal in transport containers. Wooden kneading rollers have been replaced by granite rollers made of a special close-grained porphyry.

Chromium plating, which is now used extensively in food-processing plants, as far as the author is aware, has not been much employed in margarine factories, where it might prove useful for such plant equipment as cooling drums and kneading rollers.

Hitherto, plastics have found little application for plant and utensils in margarine factories, as they must be capable of withstanding acids, alkalis, greases, salt, high and low temperatures, detergents, disinfectants, scrubbing and cleaning, etc. In addition, they must not impart any taste to the products. Such a general-utility material has not so far been produced.

Inconel is used for steam-jacketed cooking kettles. Nickel-clad steel vats are used for storage.

OLEORESINS (FROM SPICES)

Modern spice processing involves removal from a given spice of all the flavoring substances from the fruit, seed, bark, leaf, or root as the case may be and the adjustment of the proportion of volatile and nonvolatile flavoring substances to an acceptable standard.

Extraction

Materials of Construction.—In the modern plant of Wm. J. Stange Co., Chicago, stainless steel is used throughout for all equipment. (Ansel, H. R., Modern Processing of Spices, *Glass Lining,* Vol. 17, No. 4, p. 608, 1948.)

Process.—The solvent extraction method is the only means by which both volatile and oleoresinous flavoring substances can be simultaneously removed from spices. The process of extraction consists of loading by gravity chute spice ground to the proper fineness into twin stainless-steel percolators. Solvent is introduced and heated by steam jackets on the percolators. Solvent or, by this time, menstruum is drawn off into the primary still. This stainless-steel still is equipped with its own wet vacuum pump and condenser, and the solvent recovered by it is returned directly to the percolator.

When extraction is completed, the spent spice is dried in the percolator and discharged into a pneumatic conveyor leading to a cyclone and storage bin.

In the meanwhile, partially concentrated menstruum in the still has been transferred to the stainless-steel finishing still, where more accurate control of heat and vacuum is maintained during finishing operations. Finished oleoresins, free of solvents, are discharged from the still.

OLIVES

The handling and processing of highly acid and corrosive products, such as brines and other mixtures containing vinegar and salt, have always been difficult matters. There are few commercial metals that will withstand the vinegar-salt combination in green olives.

Notwithstanding the corrosive character of these combinations, they are successfully handled with 18-8 stainless steel. (Mitchell, W. M., Steel Alloys, *Food Ind.*, Vol. 7, No. 12, pp. 577–579, 1935.) But on account of the unusually corrosive nature, precautions must be observed to wash and rinse thoroughly all equipment after use; otherwise pitting may eventually occur.

Redwood tanks, too, are used in large numbers for processing of olives and their subsequent storage after processing. (California Redwood Association, *Tech. Bull.* 16–5.) New tanks should be prepared in a manner recommended by the fabricators. Many of these tanks are located out of doors in territories where they are directly exposed to long periods of excessive summer heat with low atmospheric humidities, and they are subject to intermittent operations incidental to this type of processing.

Hot salt brine used in packing plants processing olives is concentrated to 20 to 30 per cent by weight and heated to the desired temperature (160°F.) with high-silicon iron heat exchangers. Similar metal is used for pumps, valves, and fittings handling the vinegar-brine solutions.

ORANGE OIL

After experimenting with several methods for processing orange oil, the Brazilians finally settled on one improvement on the Auena. The fruit is first soaked and washed. The extractor of the machine, constructed of iron, contains the horizontal rotating disks which are covered with glass plates. The inner walls, too, are lined with glass plates. Some operators employ stainless-steel plates. Oranges are charged upon the two plates. A spray of water carries the emulsion of liberated oil into a system of strainers. This consists of several metal sieves of progressively finer mesh.

Complete separation of outflowing emulsion consisting of oil, aqueous-cell liquid, carrier water, and fine cell detritus is done by decanting in large settling tanks and centrifuging.

After standing, the effluent is pumped into a series of wooden tanks, where the fine emulsion is permitted to settle until it separates. The extraction effluent is separated in centrifuges.

The different clarified-oil lots are finally bulked into uniform lots and stored airtight in well-filled bottles.

OXALIC ACID

Oxalic acid is found in many plants in the form of its salts, and it can be made from many organic compounds by oxidation. One of the most common methods is the Goldschmidt process.

Production

Materials of Construction.—Plain cast iron and steel are slightly corroded by oxalic acid, but the rate is slow enough to make these materials the most economical to use for equipment, provided iron contamination can be tolerated.

Evaporators used in the production are generally made of cast lead or cast bronze (Cu, 90; Sn, 10). Crystallizers are made of copper with cast-bronze fittings and copper piping. Everdur can be used also.

Process.—The Goldschmidt reaction consists of heating sodium formate to give sodium oxalate. The crude material is purified by dissolving in water and adding a soluble calcium salt. The calcium oxalate that is formed, being insoluble, is filtered off and washed. It is then treated with dilute sulphuric acid to form oxalic acid and calcium sulphate. The insoluble sulphate is filtered off. The filtrate is pure oxalic acid. This can be concentrated by evaporation. The acid can then be crystallized.

Oxalic acid can also be made in a steel autoclave by reacting a caustic soda solution with carbon monoxide at 375°C. To the sodium oxalate thus formed is added milk of lime, and the remainder of the process is similar to that previously described.

It can be made from sodium formate in an autoclave. If the temperature is raised in the autoclave to 375°C., the oxalate is formed. The sodium oxalate is treated as before to convert it to pure oxalic acid.

Handling

Oxalic acid can be handled by plain cast iron and steel if slight corrosion is not objectionable.

This acid corrodes aluminum slightly; nevertheless aluminum filters and crystallizers for it and its salts have been used.

Oxalic acid solutions up to 50 per cent are being handled by stainless-steel and high-silicon iron pumps. Hard-rubber equipment is also being used to handle this acid. Durimet 20 and Worthite are said to be more resistant to oxalic acid than 18-8 stainless steel at all concentrations and temperatures. Copper and Monel are also said to be satisfactory for oxalic acid. Phenolic and vinyl copolymer resin coatings give satisfactory service.

Tenth normal and hundredth normal solutions of oxalic acid attack tin coatings of cans rapidly in the air but scarcely at all in vacuum or in an atmosphere of carbon dioxide. (Hamlin, M. L., and F. M. Turner, "Chemical Resistance of Engineering Materials," p. 72, Reinhold Publishing Corporation, New York, 1923.) The acid oxidizes more than its equivalent of tin. As for zinc, oxalic acid has scarcely any effect on the metal and indeed tends to inhibit the action of other organic acids.

Packaging

Oxalic acid is shipped in paper-lined wooden barrels and kegs, also in multiwall paper bags and fiber drums.

OXALIC ACID—SULPHURIC ACID

A chief engineer of a chemical plant reports that in one process he encounters oxalic acid (with about 1 per cent free sulphuric acid) in all concentrations from 5 to 50 per cent and all temperatures from cold to boiling. All solutions within this range are handled well by the following materials: Elcomet K for pumps and other castings; Everdur or copper for piping; zinc-free bronze for pipe fittings; Monel for certain centrifugal parts, baskets, and shafting; and lead for tank linings. Glass-lined equipment is also satisfactory.

OXIDIZING SALTS—SULPHURIC ACID

Hastelloy C will handle sulphuric acid containing oxidizing salts. (Chisholm, C. G., Hastelloy Alloys, *Chem. Eng.*, Vol. 55, No. 5, p. 238, 1948.)

OYSTERS

Government regulations require all food-handling and -processing plants to be very clean. This can generally be accomplished most easily by using special materials of construction.

Production

Materials of Construction.—Stainless steel and Monel are used in plants packing oysters.

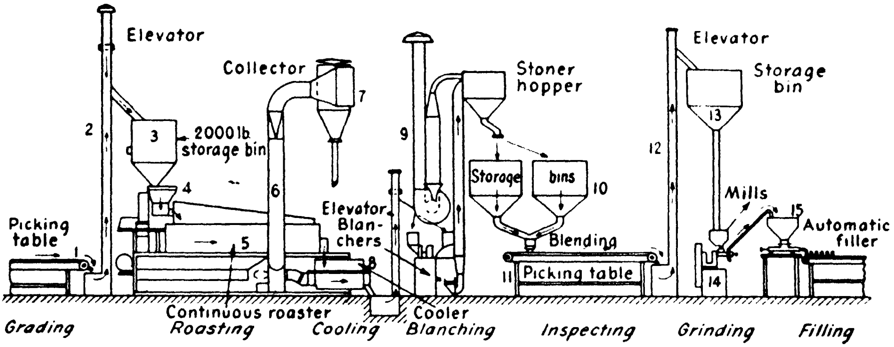
Monel is highly resistant to sea-water corrosion. This accounts for its application to a very considerable extent in the oyster-packing industry, where equipment must be able to withstand continued exposure to salt water. (LaQue, F. L., Nickel and Its Alloys, *Food Ind.*, Vol. 7, No. 12, pp. 580–582, 1935.)

The same statement might be made for stainless steel.

Process.—Oysters fresh out of the shells are put into Monel shucking pails. (Anon., From Shell to Container, *Inco*, Vol. 22, No. 2, p. 11, 1948.) The contents of the pails are dumped onto a Monel skimming table. These bivalves are carefully rinsed and inspected for shell fragments, after which they are measured into a perforated Monel container. Oysters are put into Monel aerated washing tanks. Air and water lead-in lines, as well as the tank itself, are made of Monel. After the 15-min. washing cycle the oysters are ladled out of the aerated washing tank onto the skimming table and packed for shipment. The dipper and table are made of Monel.

PEANUT BUTTER

While there are few if any corrosion problems in the peanut-butter industry, being a food industry cleanliness is demanded. And cleanliness calls for stainless steel or other special material.



Peanut butter.

1. Heavy canvas
2. Steel
3. Steel
4. Steel
5. Steel
6. Steel
7. Steel
8. Steel
9. Steel
10. Steel
11. Heavy canvas
12. Steel
13. Steel
14. Stainless steel
15. Stainless steel

Production

Materials of Construction.—Ordinary steel is all that is necessary for all pieces of equipment used for roasting, cooling, and blanching. However, the grinding of the peanuts and the filling machine are stainless steel.

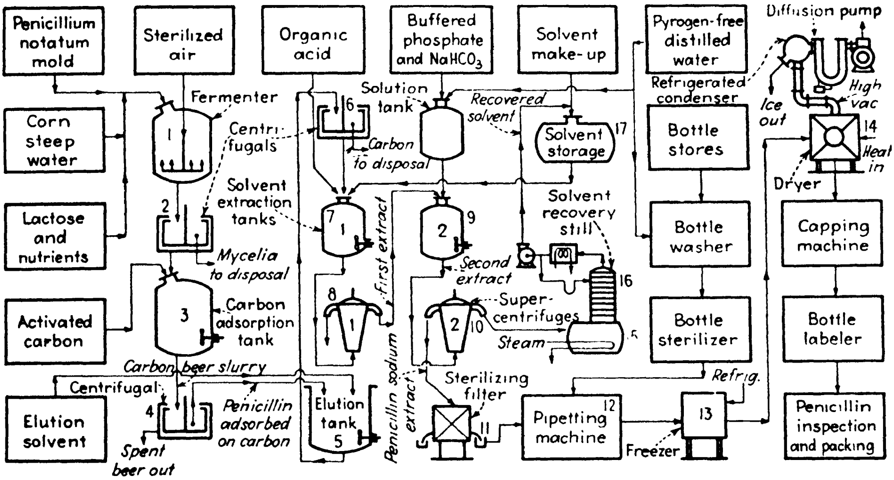
Process.—The process is relatively simple, consisting of shelling, dry roasting, and blanching the peanuts, followed by fine grinding. (Woodruff, J. G., H. H. Thompson, and S. R. Cecil, Peanut Butter, *Food Ind.*, Vol. 21, No. 2, pp. 186-191, 1949.) Salt is put in to improve the flavor, and small quantities of other materials are sometimes added, such as hydrogenated fat or glycerin to prevent oil separation, lecithin or antioxidants to control rancidity, and "secret" ingredients.

Packaging

Peanut butter is shipped in glass containers.

PENICILLIN

Several processes are used for the production of penicillin. The submerged-fermentation method is in use at the Terre Haute, Ind., plant of Commercial Solvents Corp. It is described here. (Callaham, J. R., Penicillin Large Scale Production by Deep Fermentation, *Chem. & Met. Eng.*, Vol. 51, No. 4, pp. 94–98, 1944.)



Penicillin (deep fermentation process).

1. Carbon steel, glass-lined steel
2. Stainless-steel basket
3. Stainless steel
4. Stainless-steel basket
5. Steel
6. Stainless-steel basket
7. Glass-lined steel
8. Stainless-steel bowl
9. Glass-lined steel
10. Stainless-steel bowl
11. Stainless-steel bowl
12. Stainless-steel bowl
13. Stainless-steel bowl
14. Stainless-steel bowl
15. Glass-lined steel
16. Glass-lined steel
17. Glass-lined steel

Production

Materials of Construction.—Stainless steel is used throughout the process for most of the equipment. However, a few pieces of equipment are constructed of other materials, as, for example, the fermenters, which are ordinary carbon steel, and the equipment in solvent purification, which consists of small glass-lined tanks.

Some plants prefer glass-lined steel fermenters, process kettles, distillation equipment, solvent recovery assemblies, and special equipment. Neoprene-lined valves are used.

Racks, trays, assaying cylinders, vial stoppering, turntables, automatic filling machines, and weighing rooms in the production of penicillin are of stainless-steel construction, as are numerous tanks, valves, tubing, and fittings.

Inconel is used for fermentation tanks by the deep-culture method.

Process.—Briefly, the process is divided into five steps: (1) submerged fermentation, (2) removal of mycelia and charcoal adsorption of the penicillin, (3) solvent purification and formation of the sodium salt, (4) freezing and high-vacuum drying, and (5) packaging, testing, and storage.

Corn steep liquor is diluted, and lactose up to 4 per cent is added as a nutrient. This aqueous medium is then sterilized by cooking with steam. Fermenters are constructed of carbon steel. Each fermenter batch is inoculated with pure culture of *Penicillium notatum* bred on slants in the media laboratory and germinated in seed tanks. Mash from seed tanks is put into the fermenter charge, after which the mold is allowed to grow and produce penicillin. The fermenter charge is dropped into an open-type centrifugal with a stainless-steel basket. Here the mycelia are filtered off and discarded.

Filtered beer is pumped into a closed, side-agitated, low-carbon stainless-steel adsorption tank, where it is treated with activated carbon. Penicillin and certain other constituents are adsorbed in the charcoal. Carbon beer slurry is pumped to a centrifugal having a stainless-steel basket. The carbon-penicillin is dropped into a steel elution tank.

Purification of the crude penicillin is done in a series of operations using organic solvents: (1) extraction of the penicillin from activated charcoal and removal of the charcoal, (2) partial removal of impurities by a solvent-solvent treatment of the penicillin concentrate together with a pH adjustment with acid, (3) separation of solvents and a second treatment of extract with a sodium salt and buffered phosphate, (4) separation and recovery of solvents by distillation, (5) filtration of aqueous solution of penicillin-sodium prior to filling operations.

Equipment used in the solvent purification consists of small glass-lined tanks, whereas equipment up to this point has been mostly stainless steel. The principal solvent is amyl acetate. A small amount of infusorial earth is used as a filter aid in removing the eluted charcoal in stainless-steel baskets of centrifugals.

In the first solvent-solvent extraction of penicillin concentrate, an inorganic acid is added to adjust the pH. The emulsion from this operation is put through a supercentrifuge with a stainless-steel bowl. In the second solvent extractor, aqueous sodium bicarbonate and a buffered phosphate are added. Penicillin forms a sodium salt, which is put through a second supercentrifuge with a stainless-steel bowl.

Dissolved penicillin-sodium from the final extractor is blown through a Seitz-type biological plate-and-frame filter of stainless-steel construction, where paper matte plates remove bacteria and pyrogen. The filtrate is received in a stainless-steel container known as the "final bulk container."

At this point the penicillin concentrate enters the sterile area of the plant. In fact, the operations of pyrogen filtration, bottle washing and sterilizing, filling, freezing, high-vacuum dehydration, bottle capping, labeling, and packaging are all conducted under the most sterile conditions in order to avoid product contamination.

Packaging

Packaging is done in glass bottles.

PENTACHLORETHANE

The German firm of Alexander Wacker A.G. was producing pentachlorethane among other chemicals in its plant at Burghausen. (Carpenter, G. B., Chlorinated Hydrocarbons from Acetylene, FIAT Final Report 843, Technical Industrial Intelligence Division, U.S. Department of Commerce.)

Production

Materials of Construction.—A lead-lined kettle was used. The pipe line handling chlorine to the reactor was iron lead-covered. Lead-lined crude storage tanks were used.

Process.—Pentachlorethane was made from trichlorethylene by batch chlorination in a lead-lined batch kettle. A charge of trichlorethylene containing ferric chloride was charged into a lead-lined jacketed kettle. The stirrer was not always used. The temperature of the charge was raised to a minimum of 50°C., and chlorine gas added through a lead-covered iron pipe line extending to the bottom of the tank. Maximum temperature during the reaction was 80°C., and one batch took 16 hr. for completion. Upon completion of the chlorination, the charge was pumped to lead-lined storage tanks.

PEPPERMINT OIL

In the Northwest peppermint is said to give up to 100 per cent greater yields of oil than in other regions. A continuous still for fractionating the oil has replaced small pot stills in the plant of I. P. Callison & Sons of Chehalis, Wash. (Bloomberg, R., Botanicals, *Chem. Eng.*, Vol. 56, No. 4, pp. 108–109, 1949.)

Production

Materials of Construction.—Stainless steel is used for blending tanks and storage tanks. Tin-lined copper holding tanks at the bottom of the still are used. The heads column is tin-lined copper construction as are the pipes in the still.

Process.—When the peppermint plant matures, it is cut like hay and allowed to wilt in the field until it loses about 30 per cent of its moisture. The leaves are then packed into covered wooden tubs on the farms. Steam from a small boiler is fed into the bottom through a perforated pipe, filters up through the leaves, and drives off the oil—which escapes with the steam to a condenser and then a decanter. Here the oil rises to the top and is drawn off into galvanized drums.

The drums are stored at 45°F. until needed, then taken by hand truck to the still. The oil is pumped into stainless-steel blending tanks. Blended oil is pumped into a 1,500-gal., tin-lined copper holding tank at the bottom of the still. Then another pump sends it to the "heads" column.

This column has horizontal bubble-cap plates at 1-ft. intervals. It is of tin-lined copper construction—as are the 0.5- to 4.0-in. pipes in the still. Low-pressure steam enters near the bottom and escapes at the top. Oil enters the column at one of the middle plates.

Light, low-boiling fractions in the oil rise to the top as vapors with the steam, pass through a condenser and a reflux decanter. Oil rises to the top and drains off through a weir back into the column. Water goes under a baffle plate rising from the bottom of the decanter and is piped off into a stripper. Here residual oil is boiled off and goes through a condenser to be sent back to the heads column.

Medium- and high-boiling fractions are drawn up by a pump into the "products" column; steam is again introduced at a slightly higher temperature. The process is repeated here, the residual light oils rising as vapor into the condenser, then to the decanter. Water goes to the stripper and recovered oil returns to the heads column. Finished oil is drawn off one of the upper pasteurizing plates, decanted to separate oil from the water, then piped into stainless-steel storage tanks. Bottom oils from the products column are drained off as waste tars.

Refined oil is pumped from the product storage tanks into blending tanks, then through a 15,000-rpm. centrifuge, which takes out excess moisture and solids.

Packaging

The oil is drained off into steel drums and is ready for shipment.

PERCHLORETHYLENE

Perchlorethylene is reported to have been produced in the Burghausen plant of the German firm of Alexander Wacker A.G. (Carpenter, G. B., Chlorinated Hydrocarbons from Acetylene, FIAT Final Report 843, Technical Industrial Intelligence Division, U.S. Department of Commerce.)

Production

Materials of Construction.—For most of the equipment ordinary cast iron and steel are satisfactory. Some lead-lined steel is used. The pure perchlorethylene can be stored in ordinary iron tanks.

Process.—Perchlorethylene is made from pentachlorethane by removal of 1 mole of hydrogen chloride with lime water. The equipment used and method of operation are identical with that described elsewhere for the production of trichlorethylene from tetrachlorethane. A continuous feed of pentachlorethane is fed to the iron liming tower, together with 17 per cent calcium hydroxide slurry. The bottom temperature is 110°C., and the constant-boiling mixture of pentachlorethylene and water leaves at 86°C. The reflux ratio is 1, and about 1 per cent of bottoms (mainly pentachlorethane) is recycled to the lime tower. The pure perchlorethylene is stored in iron tanks, where triethylamine is added as stabilizer.

Handling

Nickel-clad steel, nickel, and Monel are used in the construction of solvent degreasers in metal-forming plants and for stills, condensers, receivers, and piping of dry-cleaning machines. Monel condensers handle perchlorethylene vapors from distillation in its production.

Under most circumstances, perchlorethylene can be stored satisfactorily in galvanized-iron, black-iron, or ordinary steel equipment. If the perchlorethylene is properly stabilized, it can be used in the presence of air, water, and light with any of the metals that are ordinarily used at temperatures as high as 284°F. (Manufacturing Chemists Association, "Perchlorethylene," Chemical Safety Data Sheet SD-24, 1948.)

PERCHLORIC ACID

Anhydrous perchloric acid has no industrial uses and for all practical purposes is produced only by accident. Commercial perchloric acid is distributed and used either as a 60 or a 70 to 72 per cent solution in water, by weight. It is used in a large number of plants in small quantities as a special-purpose laboratory reagent. Larger quantities would be anticipated in isolated situations where perchloric acid is used for electropolishing or where it is dispensed from carboys to bottles. In these applications perchloric acid is handled and stored in glass or ceramic vessels. The I.C.C. classifies perchloric acid solutions as corrosive liquids, and shipment of concentrations in excess of 72 per cent is not permitted.

At ordinary temperatures 72 per cent acid reacts as a strong nonoxidizing acid. Contact with combustible material at elevated temperatures may cause fires or explosions. Its solvent power when hot and concentrated is extremely valuable in the digestion of samples such as stainless steel, refractory oxides, etc.

Reactions involving perchloric acid should be carried out under metal or stoneware hoods left unpainted or protected with inorganic coatings such as porcelain. (Harris, E. M., Perchloric Acid Fires, *Chem. Eng.*, Vol. 56, No. 1, pp. 116–117, 1949.)

High-silicon iron fans are used on many installations where perchloric acid fumes are handled.

Packaging

The usual containers are glass bottles and boxed carboys.

PHENOL

There is both natural and synthetic phenol. The latter is made by any one of several processes. Owing mostly to the mineral acids and alkalis used, severe corrosion problems are encountered in all processes. Therefore, a phenol plant consists of a great many different materials of construction.

Production

Materials of Construction.—In the production and handling of phenol much plain steel and some cast iron are used. This is especially true if color is not important, but they must not be used with chemically pure phenol. In addition to these common materials of construction many of the special metallic and nonmetallic materials are employed. This is particularly noticeable for pipe lines and valves, where the list includes porcelain, rubber-lined steel, glass, Haveg, nickel, and copper. Materials used for heat exchangers include glass, brass, Hastelloy B, nickel, and carbon-molybdenum steel.

Stoneware drying towers are used for the chlorine. Cast-iron chlorinators are satisfactory because the chlorine is dry. Acid is stored in rubber-lined or concrete tanks, and the dry phenol in nickel, glass-lined, or steel tanks. Process vessels are often glass-lined. One large plant uses glass-lined steel sulphonators. Glass and chrome-alloy tubing are used. For condensers, steel, copper, silver-lined steel, and brick-lined steel are preferred. Fractionating columns are made of steel, nickel, or silver-lined steel. Tantalum bayonet heaters are used in large numbers.

Worthite valves were selected in a plant using·the sulphonation process for all departments—sulphonation, fusion, acidification, distillation, and recovery processes. In another phenol plant the phenol-lime slurry has been handled by Worthite pumps for over 5 years without repair.

Nickel is commonly used for distilling columns, heat exchangers, and piping systems in production of high-purity phenol. Nickel and nickel-clad steel are used for storage tanks. Accent is on maintaining freedom from discoloration of phenol.

Inconel is used in caustic fusion with benzene sulphonic acid to produce sodium phenate in production of synthetic phenol. Inconel reactor tubes are used for reaction of monochlorbenzene and caustic soda solution at 4,000 psi. and 750°F. to produce sodium phenate in production of phenol. "L" nickel heat-exchanger tubes are used in the same process.

In the vapor-phase regenerative process special materials of construction are used in most of the equipment. (Olive, T. R., Phenol Made by Vapor Phase Regenerative Process, *Chem. & Met. Eng.*, Vol. 47, No. 11, pp. 770–775, 1940.)

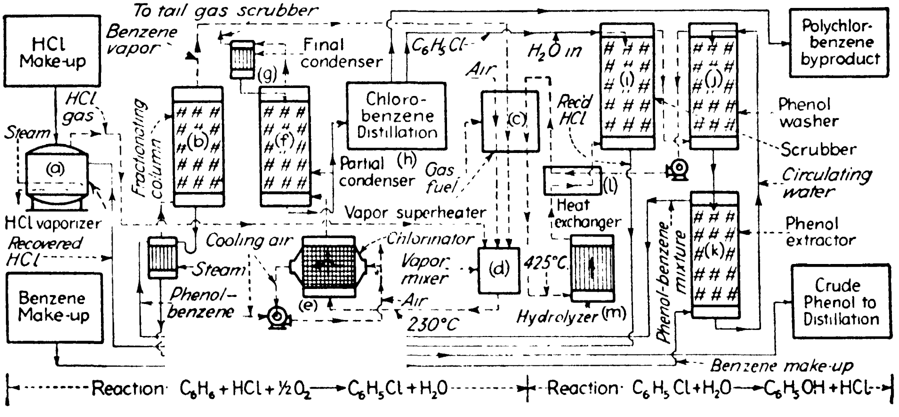
Evaporators handling HCl vapors are acidproof, brick-lined vessels equipped with tantalum bayonet heaters. HCl vapor discharges through rubber-lined pipe into a vapor mixer. It is a vertical brick-lined steel shell packed with helical tile discharging into a steel line. Converters are steel. The condenser is a steel tower equipped with a brick lining. At the top is a copper vapor take-off and copper distributing pipes for benzene, which is used to reflux the tower. At bottom a porcelain line discharges the condensate for removal of monochlor. Final condensers for unreacted benzene are of copper sheet and tube construction.

Recovered acid with a small amount of phenol is passed through brick-lined steel extractors. Benzene solution of phenol flows to a still where crude 97 per cent phenol is separated and benzene is vaporized. This still is all-steel. In the secondary phenol still, condenser tubes and all parts from there on which are in contact with phenol are of nickel to avoid contamination. The scrubber is an all-steel tower packed with stoneware raschig rings and equipped with steel distributing pipes at the top. Heat-exchange units are steel shell and tube. The oil-fired superheaters contain chrome-alloy tubes. This heat is used for the azeotropic mixture. Hydrolysis of the monochlor with steam is done in all-steel converters. HCl is recovered in brick-lined steel towers equipped with porcelain distributor pipes. The weaker acid tower contains Pyrex-glass distributors.

Pumping of acid solutions was handled by centrifugal pumps of both glass and Hastelloy B. Over a mile of chemical porcelainware in the form of pipe, valves, and raschig rings was used. Fortunately, however, a large part of both piping and equipment could be of steel, all of which was welded.

Vapor-phase Regenerative Process.—Synthetic phenol is made by this process by Durez Plastics & Chemicals, Inc., at North Tonawanda, N.Y. (*Ibid.*)

The Raschig process, as it is sometimes called, employs hydrochloric acid as an intermediate in what is virtually the direct oxidation of benzene to phenol with air. The process is in two stages, in the first of which monochlorbenzene is pro-



Synthetic phenol (vapor-phase regenerative process).

1. Acidproof brick-lined steel with tantalum heaters
2. Rubber-lined steel
3. Brick-lined steel, tile-packed
4. Steel
5. Steel
6. Brick-lined steel with copper vapor offtake and distributing pipe for benzene
7. Porcelain
8. Copper
9. Brick-lined with glass distributor
10. Chrome alloy tubes
11. Steel
12. Steel
13. Steel packed with stoneware rings
14. Steel
15. Steel

Pumps for acid solutions: glass, Hastelloy B

Pipe: steel, porcelain, glass

duced by the action of a catalyst on benzene. In the second stage, the monochlorbenzene is catalytically hydrolyzed with steam to yield phenol and regenerate the HCl. Both steps are fundamentally simple but became complex in practice owing to the need for separating and recovering unreacted materials and the regenerated HCl which circulates in the process.

It may be considered that the process starts with the vapor superheater. Benzene vapor, HCl, and air mixture are drawn into a converter by suction of a fan at the proper temperature for reaction. The chlorobenzene formed (with polychlorbenzene) condenses in a partial condenser, while the unreacted benzene condenses and returns to the process in a final condenser. The monochlor after purification is vaporized into a second stage of the process, where it is circulated with steam through a series of towers, heat exchangers, a superheater, and a converter, in the last being in part hydrolyzed to phenol and HCl. The HCl is condensed in a partial condenser, then extracted with benzene to remove what phenol it carries, and returned to the first-stage process to be revaporized. The phenol in circulation is first dissolved in water in a scrubber, then extracted by benzene from the water, the water returning to the scrubber for further duty. The combined benzene extracts of phenol are pumped to a fractionating column in the first stage, where the benzene is vaporized for the first-stage process, while the crude phenol is discharged for final two-stage distillation to produce the finished product.

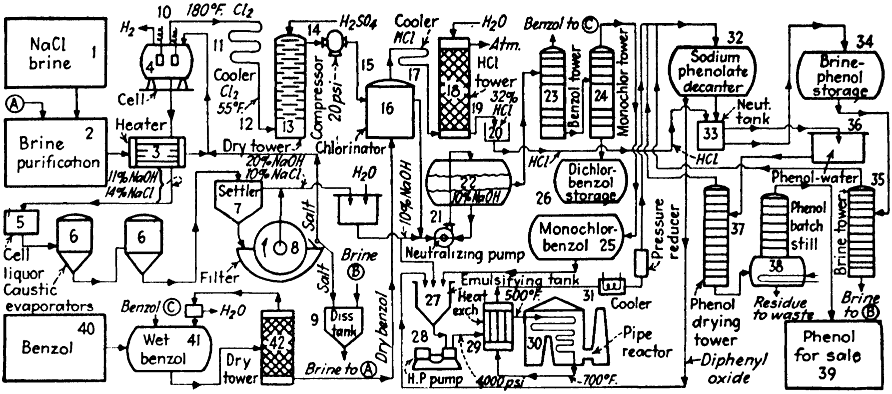
Monochlorbenzene Process.—Among the plants in this country using this process is General Electric's Pittsfield, Mass., plant, which produces phenol by chlorinating benzene, a method that will be described here. (Lee, J. A., Phenol from Monochlorbenzene, *Chem. Eng.*, Vol. 54, No. 9, pp. 122–124, 1947.)

The monochlorbenzene method, in brief, consists of chlorinating benzene to monochlorbenzene and hydrolyzing this intermediate to phenol. The chlorine and caustic soda required in the process are made in electrolytic cells. The latter is concentrated to 20 per cent and separated from salt on a rotary vacuum filter with a nickel screen. In a storage tank it is diluted to 10 per cent and held for use in hydrolyzing the monochlorbenzene. Chlorine leaves the cell by means of a stoneware pipe line connected to a header. It is cooled in a glass heat exchanger and leaves through stoneware lines. The gas is then dried in a stoneware tower by allowing sulphuric acid to come in contact with the gas in countercurrent flow. After drying, the gas passes through plain steel pipe lines to compressors. It goes directly through a steel pipe line to the chlorinator, a cast-iron kettle. Here it comes into contact with benzene dried by distillation and pumped continuously to the chlorinator. The benzene is chlorinated. Every effort is made to keep the entire system dry so as to avoid corrosion and to prevent leaks in the equipment.

Gases leave the chlorinator at 180°F. and are cooled in a shell and tube heat exchanger. Brass and Hastelloy B have been found by experience to be more satisfactory than plain steel, for the latter is most apt to foul up on the water side and thus lower the heat-transfer rate. Cooled gases go to a Karbate-tantalum absorber, where they are absorbed in water to form 32 to 33 per cent hydrochloric acid employed to neutralize sodium phenolate in the formation of phenol.

Acid is stored either in rubber-lined steel tanks or in concrete tanks lined with brick and sulphur-base cement. For acid lines from the absorber to the storage tanks porcelain, glass, and Haveg have been found to be satisfactory.

The liquid leaving the chlorinator is composed of unreacted benzene, monochlorbenzene, and dichlorbenzenes. It is first neutralized with caustic by contact in a centrifugal high-speed pump, then it goes to the chlorinated-products steel storage tank from which the clear layer is decanted and pumped continuously to the benzene tower. Chlorbenzenes are removed from the bottom of the column and are pumped to another column, the monochlorbenzene tower. The monochlor is distilled off and goes to a storage tank; the dichlors are drained off and sold as crude material. These two standard bubble-cap towers operate together, the bottom product from the first feeding the second.



Synthetic phenol (monochlorbenzene process).

1. Concrete
2. Steel
3. Steel
4. Concrete top, steel tank
5. Steel
6. Steel
7. Steel
8. Nickel screen
9. Steel
10. Chemical stoneware
11. Glass
12. Stoneware
13. Stoneware
14. Plain-steel pipe and compressor
15. Plain steel
16. Cast iron
17. Brass, Hastelloy B
18. Karbate and tantalum
19. Porcelain, glass, Haveg
20. Rubber-lined steel, brick-lined concrete
21. Cast iron
22–28. Steel
29. Carbon-moly steel
30. Carbon-moly steel
31. Steel
32. Steel
33. Enamel-lined
34–42. Steel

Monochlorbenzene and caustic are continuously added and mixed in the emulsifying tank. In the same tank is mixed the diphenyl ether, which forms as a by-product in the reactor. This mixture of the three goes to the high-pressure pump and is sent on its way at a pressure of 4,000 psi. In the carbon-molybdenum-steel heat exchanger the temperature of the mixture is raised to 500°F. It then goes to the reactor, and the temperature is further increased to 700°F. Formerly, carbon-molybdenum steel was used, but since the corrosion rate is high, other materials are being tried with very considerable success. Substantially all monochlor is reacted to sodium phenolate, diphenyl ether, or high-boiling residues.

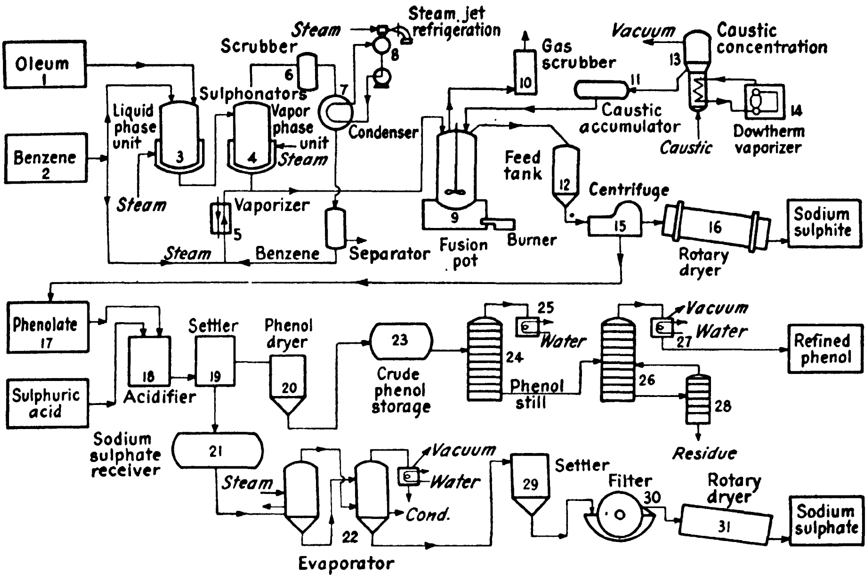
From the reactor the mixture is cooled, pressure is reduced to atmospheric, and the mixture goes to the decanter, where the diphenyl ether is separated from the sodium phenolate. The former is recycled back to the heater via the emulsifier. The sodium phenolate is continuously neutralized with the hydrochloric acid from the chlorinator in a glass-lined tank equipped with a stirrer.

Two layers are formed by this reaction, a brine layer and a phenol-water layer. The former contains sodium chloride and phenol. The phenol in the brine layer is recovered by distillation in a tower. This weak brine from the tower is filtered through sand beds to remove material in suspension and then made slightly acid. Next it is passed through activated carbon to remove traces of primary phenol and other organic material. Water-phenol comes off the top of the tower and goes to the sodium phenolate storage tank. The phenol-water goes to the continuous-distillation tower. All water and the small volume of phenol go off overhead to the sodium phenolate storage tank. The bottom product is the dry phenol and high-boiling residues. These pass to the batch kettle of a phenol tower, which operates continuously until, when the batch kettle is drained, it becomes full of residue. In other words, the phenol still operates semicontinuously under vacuum. Pure phenol goes off overhead to the steel storage tank.

Sulphonation Process.—A typical plant using this process is the Reichhold Chemicals, Inc., plant at Tuscaloosa, Ala. (Weiss, J. M., Synthetic Phenol Production in Alabama, *Heat Eng.*, October, November, December, 1944.) The sulphonation of the benzene is performed in two steps, the first operation with the benzene in liquid phase, the second with it in vapor phase. The liquid-phase sulphonator is charged with benzene and 9.5 per cent oleum fed in at a controlled rate which governs the temperature of the reaction. Upon the completion of the presulphonation, the mixed-acid charge is transferred to the vapor-phase sulphonator and the reaction completed at a higher temperature with the introduction of vaporized benzene, which is continuously fed in below the liquid level of the charge. The finished benzene sulphonic acids drop by gravity to a storage tank to be kept until used in the fusion section.

Vapor from the sulphonator is discharged through a vapor-purifying device, where it is scrubbed free of acids, then goes to a benzene condenser. The condensed water and benzene flow to a gravity decanter, where a rough separation is made. The wet benzene is subjected to a drying operation, and the dry product passed to working storage from which it is drawn for the vapor-phase sulphonation requirements.

The reaction of the product of the sulphonation process, benzene sulphonic acid, with caustic soda is accomplished in batch fusion pots, which are directly heated by fuel oil. The fusion pots are charged with concentrated caustic soda solution, heat is applied, and the residual moisture driven off. The charge is molten, and the benzene sulphonic acid is gradually introduced. Upon completion of the fusion the products, sodium phenate with sodium sulphite and other minor by-products, are diluted by admitting water. This first lowers the temperature of



Phenol (sulphonation process).

1. Steel
2. Steel
3. Cast iron
4. Cast iron
5. Steel
6. Cast iron and steel
7. Steel
8. Steel
9. Cast nickel iron
10. Steel
11. Steel
12. Steel
13. Nickel
14. Steel
15. Steel
16. Steel
17. Steel
18. Lead-lined
19. Steel
20. Lead-lined
21. Steel
22. Steel
23. Steel
24. Steel
25. Steel
26. Steel
27. 18-8 stainless steel
28. Steel
29. Steel
30. Steel and Monel
31. Steel

the molten mass, then dissolves it, with the exception of the sodium sulphite which remains in suspension.

A caustic concentrator heated by a Dowtherm vaporizer concentrates dilute commercial solution and thus supplies concentrated caustic solution for charging the fusion pots. In addition, the vaporizer supplies heat for jacketing the concentrated caustic lines leading from caustic storage to the fusion pots. Jacketing is necessary, as concentrated caustic solution is characterized by a relatively high solidification temperature.

The phenate solution, with its accompanying sodium sulphite salts in suspension, is transferred to a filter feed tank. This tank is mechanically agitated to maintain the salts in suspension, and the charge is fed to a continuous centrifugal machine where the solids are separated from the strong phenate solution. These salt crystals are subsequently dried in a rotary, steam-heated dryer.

The salt-free phenate solution then passes to the acidification section, where it is treated with dilute sulphuric acid. This reaction frees the phenol and produces the by-product, sodium sulphate, the mixture consisting of crude, wet phenol and a solution of sodium sulphate. This mass is pumped to a settling tank where the crude, wet phenol and the sodium sulphate solution are drawn off and pumped to storage while the wet phenol is pumped to a dryer where it is treated with a moderately concentrated sulphuric acid to remove the greater part of the dissolved water.

Dilute acid settles out, is drawn off and returned to the acidifier. Any acid remaining in the dried crude phenol is neutralized by the addition of alkali, and the crude phenol pumped to storage.

The crude phenol, containing some water as well as small percentages of various organic impurities, is concentrated and purified in a special continuous fractional distillation unit.

Handling

Where color is not important, plain iron and steel can be used with phenol; however, when color is objectionable, special materials of construction are a necessity.

The phenols, including phenol itself, and their water solutions are generally without appreciable harmful action on aluminum at room temperature. At temperatures around 150°C. phenol will react with aluminum after an initial period possibly because of the removal of moisture from the phenol under these elevated-temperature conditions. Aqueous solutions of phenol have very little action on aluminum up to 100°C. at least.

Worthite valves, pumps, and other equipment are being used to handle phenol at 370°F. Durimet 20 is resistant at all concentrations and temperatures, it has been reported.

Nickel and nickel alloys are generally used in the purification stages of phenol for fractionating columns, condensers, piping, and tankage. Monel reboilers are used in separating phenol from oil in phenol refining of lubricating oil.

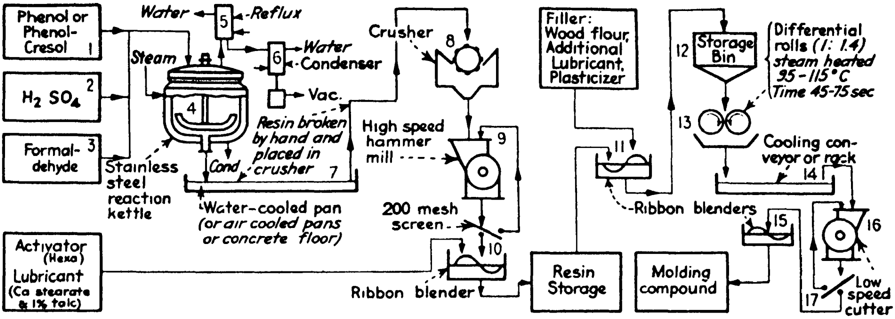
Aluminum equipment is used in many ways in contact with phenol. At elevated temperatures a small trace of water should be present, which acts as an effective inhibitor. Aluminum kettles are used to make phenolic resins.

Packaging

Nickel-lined or nickel-clad steel tank cars are used for shipping phenol. Plain steel tank cars can be used if discoloration is not objectionable. Galvanized, tin-lined, or aluminum drums are in use. Boxed glass carboys also are used.

PHENOLIC RESINS

Phenol-formaldehyde resins have long been one of the most widely used types and are produced by many companies. The process is now more or less standard except that both alkaline and acid catalysts are employed.



Phenolic resins.

1. Steel, aluminum
2. Steel
3. Rubber-lined steel, aluminum
4. Steel, stainless steel, copper, nickel-clad, cast iron, Monel
5. Stainless steel, copper, Monel
6. Stainless steel, copper, Monel
7. Steel, concrete
8. Steel
9. Steel
10. Steel
11. Steel
12. Steel
13. Steel
14. Steel
15. Steel
16. Steel
17. Steel

Production

Materials of Construction.—The formaldehyde is stored in rubber-lined steel, stainless steel, or aluminum. Some plants use the last for weigh tanks for the raw materials. The reactor material varies in the many plants. The metals that are used include steel, stainless steel, cast iron, copper, Monel, and nickel-clad steel. Condensers are copper, Monel, or stainless steel. The resin is run from the reactors into concrete or steel pans to cool. From this point on, the equipment is ordinary steel, except for the manganese-steel crushing and grinding equipment.

Process.—In what is probably a typical resin plant the phenol and formaldehyde raw materials are stored in outdoor steel tanks, of which those for formaldehyde are rubber-lined to prevent corrosion. (Callaham, J. R., Modern Plant Makes Phenolic Resins at Springfield, *Chem. & Met. Eng.*, Vol. 48, No. 6, pp. 88–90, 1941.) Pumps operated by remote control are used for transferring materials from storage to the charging feed tanks on the top floor. Manufacture starts in steam-jacketed steel kettles. Into these kettles go the phenol, formaldehyde, and a trace of sulphuric acid to catalyze the reaction. Steam of 150 lb.

pressure is used in the jacket. The kettles are subjected to 29½ in. vacuum. The materials are churned.

When a siruplike mass is formed, it is run out of the bottom of the reactor onto a steel floor, which is really a pan. After cooling, the solid resin is broken up and sent to the basement bins.

A rotary crusher reduces it to ½-in. particle size. A steel roller mill then reduces the particles to 200 mesh. In a mixer a lubricant is added to prevent sticking during molding. Also added here, in the two-stage resins, is the hardening agent, such as hexamethylenetetramine.

This resin compound is now ready for processing into molding material. The resin, coloring matter, and filler are mixed in ribbon-type mixers for black or brown mixes and ball mills for colored mixes. The compound is passed through heated steel rolls. Heat and mastication soften the resin, and all ingredients are homogenized. A saw-tooth crusher reduces it to chips. After grinding and screening, the molding powder is stored in bins.

Packaging

Phenolic molding powder is shipped in steel drums.

PHENYLACETIC ACID

For siphons and short pipe lines, an engineer reports that his company employs Saran tubing. The chemical resistance of this tubing appears to be good enough to permit its use in moving the acid. His only objection is that it becomes brittle at elevated temperatures. Live steam, for example, has been carried in Saran tubing (at low pressure, of course), and at that temperature the tubing becomes brittle in a rather short time.

In another plant it is necessary to vaporize glacial acetic acid containing a small amount of phenylacetic acid and to superheat it to a temperature of about 600°F. The equipment in contact with this hot, airless vapor is built of Type 316 stainless steel. There is a small amount of corrosion at the weld points, but otherwise the stainless steel is satisfactorily resistant to attack.

β-PHENYLETHYL ALCOHOL

A crude grade of β-phenylethyl alcohol was made during the war by the Germans. (Adams, D. A. W., and W. Baird, Some Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.)

Production

Materials of Construction.—The equipment consisted of (1) an iron vessel with blade agitator and brine cooling bath; (2) a measuring vessel for benzene; (3) pressure vessel for liquid ethylene oxide; (4) column for exit gases filled with raschig rings made of Haveg (water trickles down the column and is removed at the bottom by means of a siphon), washer for 20 per cent caustic solution for neutralizing any acidity in the nitrogen, and drying column with calcium chloride for drying the nitrogen; (5) iron lead-lined separator, lead-covered stirrer, and lead cooling coils; (6) iron still with copper heating coils and stirrer, short column, condenser, etc.; (7) cast-iron still with copper heating coils for vacuum distillation of phenylethyl alcohol; (8) iron vessel for storing the recovered benzene.

Process.—This alcohol is produced by the reaction of ethylene oxide with benzene in the presence of aluminum chloride. The condensation pan is charged with benzene, and the brine circulation is started in the jacket. The temperature is allowed to fall to 7°C., and aluminum chloride added. The vessel is swept out with nitrogen, and the pressure built up to 0.5 atm. This is released, and the vessel is again swept out with nitrogen. The pressure is built up to 0.2 atm. The temperature is lowered to 5°C., and the introduction of ethylene oxide started as liquid by means of nitrogen pressure. The ethylene oxide is added. Agitation is then continued for 1 hr.

The batch is then blown with nitrogen into the separating cylinder containing water. The cylinder is coil-cooled, and the temperature not allowed to rise above 35°C. After agitating, the batch is allowed to settle. The acid layer is run off, and the benzene layer blown into the still. Here the benzene is distilled off at atmospheric pressure.

The residue is blown to the vacuum still and distilled at 15 to 25 mm. The forerunnings, collected up to 110°C., are run back into the next batch in the separating cylinder. The main fraction distils at 110 to 125°.

The benzene from the first distillation is stirred with water and 25 per cent caustic soda solution under reflux. The benzene is then steam-distilled off, charged back, washed with cold water, and finally again distilled. The benzene is separated from the water layer and dried over calcium chloride. It is then reused.

PHENYL ISOCYANATE

It has been reported that the German I.G. Farben. was producing phenyl isocyanate at its Uerdingen plant. (Adams, D. A. W., and W. Baird, Some Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.)

Production

Materials of Construction.—The reaction kettle consists of a lead-lined pan with a blade stirrer and jacketed for 20 atm. steam. It carries a lead-lined column packed with porcelain raschig rings, and on top of the column there is a dephlegmator leading, as required, to a ring-packed water scrubber and then to a kettle containing ethylaniline or to a steam ejector pump via a condenser with receiver and a caustic scrubber.

It was necessary to repair the lead lining in the kettle. No other material was found satisfactory, but possibly a tile-lined reactor with a silver heating coil might be better, though silver was also reported to have been attacked, according to the Germans. But glass-lined steel would be superior to either lead or tile for this purpose.

Process.—The pan is charged with chlornaphthalene and heated to 150 to 160°C. Aniline and phosgene warmed to 40°C. are then fed in simultaneously at as nearly proportional rates as possible, the aniline running in at the top of the pan and the phosgene being fed to the bottom of the pan. The addition takes about 16 hr., then the reaction mixture is stirred a further 3 hr. at 160°C. Normally 10 to 15 per cent phosgene is present, and when it rises to 30 per cent, the reaction is considered to be ended.

The exit gases pass through the column and condenser, then via pipe line at 40° to the water scrubber to remove hydrochloric acid, the phosgene passing on to be absorbed in ethylaniline.

When the reaction is ended, dry air or nitrogen is blown through to remove residual hydrochloric acid and phosgene. Vacuum is then applied slowly to distil over the phenyl isocyanate, the pressure being eventually about 40 mm. and the temperature 100 to 120°C.

The crude isocyanate contains hydrochloric acid and some chlornaphthalene. It is redistilled, using a ring-packed column, at 25 to 40 mm., the temperature being 60 to 80°C. depending on the pressure. A forerun is taken to remove hydrochloric acid, then the main fraction is distilled over. The forerun is charged to the next distillation batch.

The final product is 99.5 to 99.9 per cent pure and contains less than 0.05 per cent chlorine.

PHENYLMERCURIC ACETATE

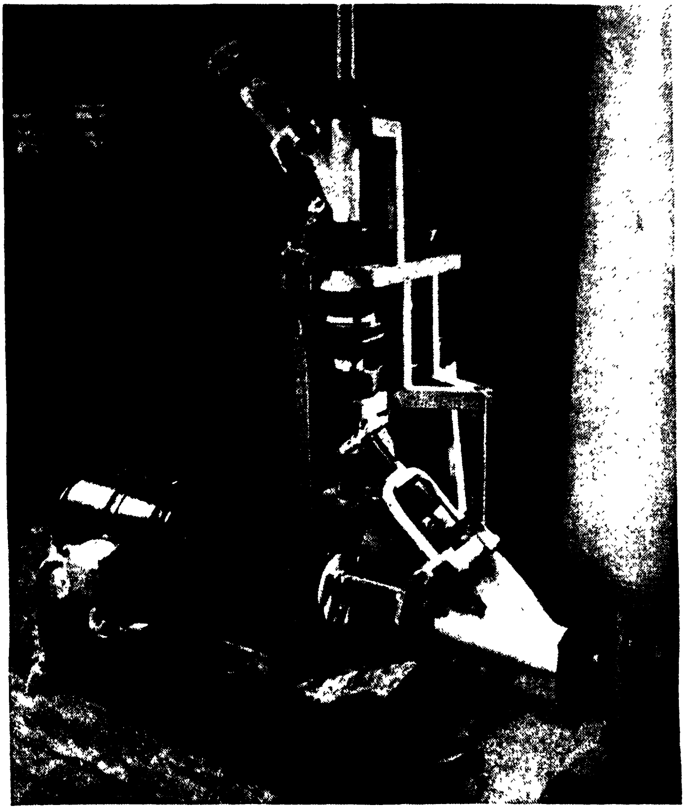
It was reported after the Second World War that I.G. Farben. had made phenylmercuric acetate at Elberfeld and Leverkusen. (Adams, D. A. W., and W. Baird, Some Miscellaneous Organic Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.) The Leverkusen process was considered the more economical, but the plant was unsuitable to handle such toxic material.

Production

Materials of Construction.—The reacting kettle was constructed of glass-lined steel. It was equipped with a stainless-steel (Cr, 18; Ni, 8; Mo, 3) stirrer. The condenser was made of the same type of stainless steel or of earthenware. Other parts of the equipment were fabricated of stainless steel or glass-lined steel.

Elberfeld Process.—Mercuric oxide, benzene, and acetic acid were charged to a glass-lined kettle carrying a stainless-steel blade stirrer and subjected to azeotropic distillation at about 78°C. for 13 hr. Aqueous acetic acid separated out as the bottom layer of the condensate during the reaction and was run off. The completion of mercuration was shown by adding caustic to an aqueous extract of the batch. No precipitation of mercuric hydroxide should have been formed.

The excess benzene and acetic acid were then distilled off firstly without vacuum. The first 150 to 200 kg. separated as a small aqueous layer, which was run off, and then about 550 to 580 kg. was taken off up to about 110°C. The temperature was reduced, and the rest distilled off at 75 to 95°C. in vacuum. The distillate was initially mainly benzene, and that obtained under vacuum was essentially acetic acid.



Hard-rubber centrifugal pump on which a combination of glass piping and porcelain valves is used. These and many other special materials were used at the Clinton Engineer Works, Oak Ridge, Tenn.

The residue in the kettle was stirred with warm water, then cold water was added. Any adherent crust had to be scraped off. Residual acetic acid was neutralized with chloride-free caustic to a faint but definite red end point on litmus paper. The batch was then blown to an enclosed, enameled nutsche, where it was washed with water, well drained and then washed with 2 per cent soda ash solution. The product was dried on trays in an oven at about 90°C. Phenylmercuric chloride was recovered from the filtrate and washings by addition of salt. This was dried with the main product, and the whole mixed and ground together. The recovered benzene-acetic acid and acetic acid were reused after estimation of their composition.

Leverkusen Process.—Dry benzene and 96 per cent acetic acid were charged to the pan, and mercuric oxide was added with stirring. The temperature was raised to 97 to 98°C. in 1 hr., and azeotropic distillation of the water from the reaction continued for 15 hr. After testing to check that mercuration was complete, benzene was distilled off during 5 hr. at normal pressure up to 90°C. Then the acetic acid was removed up to 90° in vacuum during about 2 hr.

The residual product in the pan was blown into water, the acetic acid neutralized to pH 4.5 to 5, and the precipitated product filtered off and dried. The filtrate from three batches was collected, and mercury compounds precipitated as chlorides by salting.

PHOSPHORIC ACID

The problems of corrosion in the production of phosphoric acid can generally be considered in two phases: (1) production by the thermic process, electric furnace, and (2) production by the wet processes, (*a*) weak-acid process and (*b*) strong-acid process.

The corrosion problems are indeed complex. In the manufacture of this acid from phosphoric rock, the fluorine content is even more troublesome than the phosphoric acid. The sulphuric acid used in treating the rock gives its share of trouble. The materials of construction problem is further complicated by the abrasive character of the gypsum slurries that must be handled. Handling of pure phosphoric acid is somewhat simpler, though not an easy matter.

Production

Materials of Construction.—Materials employed in the production and handling of the acid are numerous. Wood has long been used for the fabrication of much of the equipment. Lead has been very generally used in castings or as a covering. Rubber-lined and -covered steel is frequently employed. The linings are often protected against abrasion by an acidproof brick lining. Stainless steel, carbon, Karbate, high-silicon iron, and several alloys such as Worthite, Durimet, Hastelloys, and Illium are used. Among the nonmetallic materials often specified are Saran, Haveg, chemical stoneware, and vitreous silica. The most recent development is the use of graphite combustion chambers for the burning of liquid phosphorus in the electric-furnace process. Several have been installed in the past year or two.

The piping arrangement and type of pipe and valves to be used are of paramount importance in phosphoric acid plants. A poor arrangement can cause considerable grief and loss of production. From a corrosive standpoint, lead or lead-lined steel pipes are entirely satisfactory. With some of the solutions encountered, however, they will very rapidly fill up with a crystalline scale and must be arranged so that they can be readily taken down for cleaning. For this reason it has been found preferable in some cases to use rubber hose. In this way sharp turns are avoided and crystallization can frequently be broken down and removed without disconnecting the line by simply flexing the hose at the point of restriction. Rubber-lined steel pipe is economical and has several advantages.

In operation under pressure or above operating floors, however, the use of rubber hose introduces a hazard. There have been cases where they have burst. For this service the hose should be of a special, acid-resisting construction, adapted to high-temperature service and provided with molded and reinforced flanges like cast-metal pipe. A preferred type is known as "pinch-valve hose" with which it is possible to use steel clamps in place of ordinary valves. The hose should be heavily reinforced, and the suction line protected against collapse by spirally laid, steel reinforcing. It is also necessary to have the outside of the hose thoroughly protected by a heavy, tough covering of acid-resisting rubber.

If rubber-lined or lead pipe is employed, a lubricated, special stainless-steel, plug cock is very satisfactory, especially for sludges. Cocks of this type can also be obtained in rubber-lined construction. Stainless-steel globe Y valves are excellent for noncrystallizing solutions, and lead Y valves are suitable for weak, noncrystallizing acids. Pinch-type valves are inexpensive and very satisfactory.

Very close control of the rate of feeding rock and sulphuric acid is of great importance in plants of this type, as well as control of the return of weak acid to the reaction. A rotating, scoop feeder of novel design, known as the "Howard acid feeder," has been generally used in plants for this purpose. The submerged parts are made of hard lead or rubber-covered steel, and the mechanism is installed in a welded-steel tank for sulphuric acid feeding and in a lead-lined or, preferably, rubber-lined steel tank for phosphoric acid. Flowmeters, siphon feeders, tanks, and other such devices have been tried, but the crystallizing and corrosive nature of these solutions make anything but the very simplest type of feeder most undesirable.

Various types of evaporators are used based on the fuel available. Submerged combustion units have been tried where cheap natural gas was available. Burners are of stainless steel, tanks steel-lined with carbon bricks set in resin cement, and covers and vapor piping of stainless steel. Where fuel oil is the preferred fuel, hot gases can be produced in a separate combustion chamber and then blown through the acid. Carbon brick-lined tanks and alloy-steel distributors are used. Where low-pressure steam is available, vacuum evaporators are preferred operated in accordance with Dorr's continuous-recirculation scheme. Evaporator bodies are of cast lead and rubber-lined steel, vapor piping is rubber-lined, tube sheets are hard lead, and tubes are Karbate with rubber gaskets.

In the strong-acid process, cooling of the reaction slurry is required. For this purpose low-pressure air is bubbled through the slurry. The air distributors are of cast lead with stainless stay bolts or stainless-steel construction throughout.

Fumes are evolved at several stages in the process, yet excellent working conditions can be maintained by the liberal use of fume ducts leading to scrubbing towers or to the atmosphere. The ducts themselves may be made of wood protected with asphalt or preferably of sheet steel lined with rubber. The exhaust fans should be of acid-resisting construction. Rubber-covered fans are satisfactory. Scrubbing towers can be wood or acidproof-brick construction.

All operating floors should be very carefully classified as to whether they are subject to acid spillage or not. This acid plays havoc with floors and other structures. The best flooring is a well-drained concrete floor protected by asphalt, acidproof brick, or a resin-base paint wherever subjected to spills. Walkways and stair treads may be of steel grating. Steel building columns or equipment foundations should be thoroughly protected against acid spill. Columns where they pass through floors should be protected with a concrete asphalted base. All floors should be curbed, sloped, and drained so that they can be thoroughly flushed with water. (Weber, W. C., Phosphoric Acid Imposes Severe Corrosive Burden, *Chem. & Met. Eng.*, Vol. 39, No. 10, pp. 542–545, 1932.)

For information on corrosion problems in the wet process the author has drawn on the article by Weber who, together with the Dorr Co., has kindly reviewed and brought up to date that portion of the article dealing with the wet process.

Acid produced from phosphate rock by the wet process contains small percentages of sulphuric and hydrofluosilicic acids. The latter is very troublesome especially because of its volatile reaction products. Another complication is that the solutions are saturated with gypsum and usually sodium and sometimes potassium fluosilicates with their steep solubility curves and troublesome crystallization.

The rock is customarily ground dry with air separation, although some plants have used wet grinding in pebble mills, using weak phosphoric acid as a grinding solution. In the latter case the shell, feed drum, and discharge bell of the tube mill are constructed of iron or steel. All interior surfaces are protected by a rubber lining. Longitudinal hardwood strips are applied directly over the rubber lining, and upon this layer of wood is laid the final lining of silica blocks set in acidproof cement. For the grinding medium are selected flint pebbles, while the manhole, frame saddle, cover, and in some cases the feed scoop are stainless steel. This construction, used in both strong and weak plants, provide, (1) an impervious rubber lining to protect metal parts from corrosion, (2) a layer of wood to act as a buffer between the silica lining and the rubber-coated shell, and (3) a lining of blocks to stand the abrasion and shock of the cascading charge and pebbles. It is preferable to use a rubber-covered drum type of feeder.

The agitation tanks may be of steel, wood, or concrete. In the case of wood tanks these must be lead-lined, and the lead should be protected from abrasion and fluorine attack by wood or, preferably, a lining of acid-resisting brick. Steel tanks may be lead- or rubber-lined. The use of light stainless-steel tanks appears increasingly attractive. Concrete tanks have been successfully lined with a double layer of acid-resisting bricks set in acid-resisting cement. Steel is the preferred tank construction except where the other materials are cheaper. Tank covers can best be constructed of wood protected with asphalt. Fume ducts can be of wood, but rubber-lined steel is preferable. The Dorr type of agitator, using combined air and mechanical agitation, was formerly used in weak-acid plants, but special designs of mechanical agitators using propellers or impellers are now preferred. Agitator shafts and impellers may be of rubber-covered construction or stainless steel. A number of factors affect the choice of the best design and materials of construction for the agitators.

Thickener tanks may be of wood, steel, or concrete construction. If of wood or steel, they are lead-lined and provided with wood covers. Concrete tanks may be lined with acid-resisting bricks set in acid-resisting cement. For very weak acids wood may be used for the shafts, arms, and braces of the thickener mechanisms, all joined together with bolts and fittings of special stainless steel and with raking blades of plumbalum. For strong acids lead-covered steel or, even better, rubber-covered steel would be entirely satisfactory. Blades are stainless steel.

For filtering weak acid as was often the case at the end of decantation plants, drum filters of the Oliver type were used. The drum or shell was of wood.

For the direct filtration of strong acid in the Dorrco strong-acid process, the Dorrco type of internal drum filters was originally used. These were of rubber-covered construction, but in later designs the shell is lead-lined with wood drainage boards and stainless-steel clamp bars and bolts. The valve has a stainless-steel seat and antimonial lead cover. Vinyon backing and filter cloths are used.

Present-day designs employing this type of strong-acid process prefer the use of horizontal-type belt or table filters. The belt filters use rubber or neoprene belts supported on a stainless-steel suction box and hard-lead deck. The table filters are lead-lined steel with extruded antimonial lead-backing grids and panel division strips. The cloths are held in place by asbestos rope caulking in hard-lead grooves. The valves and valve covers are rubber-covered steel with a plastic wear plate. Both types of filters use synthetic filter cloths.

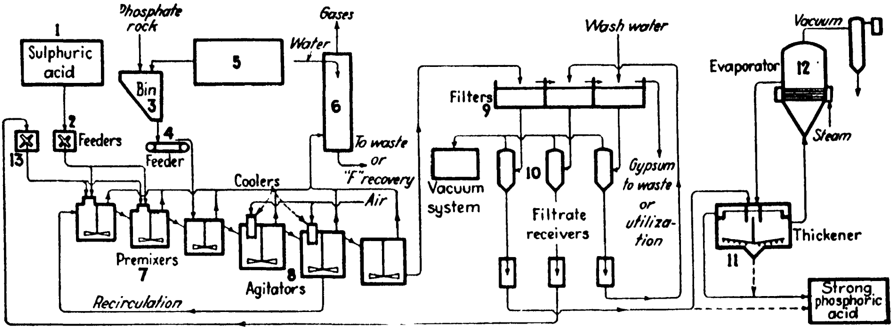
In the weak-acid process, thickener underflows are handled by diaphragm pumps. The bodies are built of hard lead or preferably of rubber-covered steel. The diaphragms are of rubber-cord construction, and both studs and plunger are of stainless steel. Lead-impregnated rubber ball valves and rubber valve seats are used. Elsewhere throughout the plants acid sludges are handled by pumps of the centrifugal type. The sand type of pump without packing gland, such as the Wilfley, is greatly to be preferred, and pumps of this type with rubber-lined steel casings, special stainless-steel runners and shafts, and an all-stainless construction have been very satisfactory.

Centrifugal pumps are used exclusively for solutions. In the case of weak acid, hard-lead casings with runners of Illium have been used successfully, but all-stainless-steel construction or Worthite or similar alloys are most satisfactory and must be used for strong acid. This question of the proper choice of pump is vital to the success of a wet-process plant.

Troughs and launders are, of course, simpler and more accessible than closed pipe lines. Good phosphoric acid engineering suggests their use wherever practicable. Lead-lined wood construction is satisfactory for solutions, but an additional lining of abrasive-resisting brick should be used where sludges are to be handled or where concentrated fluorine fumes are present.

Piping for sludges should be rubber-lined, and for solutions may be lead, lead-lined steel, rubber hose, or rubber-lined steel.

Wet Process.—This process, also known as the "sulphuric acid method," consists of treating phosphate rock with sulphuric acid. One modification formerly used, the weak-acid process (Weber, W. C., *Chem. Markets*, April, 1930), produces a phosphoric acid containing up to 22 per cent P_2O_5, but this has been almost entirely supplanted by the strong-acid process (Weber, W. C., *Chem. & Met. Eng.*, Vol. 39, No. 12, pp. 659–662, 1932), which produces directly an acid containing up to 34 per cent P_2O_5.



Phosphoric acid (Dorr strong-acid process).

1. Steel or lead-lined
2. Steel or lead-lined
3. Steel
4. Rubber
5. Steel
6. Asphalted wood, acid brick
7. Tank: lead or brick-lined steel or wood. Mechanism: stainless steel.
8. Tanks: lead-lined wood, lead or rubber-lined steel protected by acid brick or wood, acid brick and concrete, stainless steel. Mechanism: rubber-covered or stainless steel.
9. Rubber, lead, wood, stainless steel, synthetic-resin cloth
10. Lead or rubber-lined steel
11. Tank: lead-lined wood, acid brick-lined concrete. Mechanism: wood, lead, rubber-covered steel.
12. Lead, rubber covered, stainless steel, Karbate tubes
13. Lead-lined wood or steel, brick-lined concrete

Pumps: steel, rubber-lined steel casings, and stainless-steel runners and shafts; hard-lead casings with runners of Illium; all stainless steel, Worthite, Hastelloy B

Valves: rubber, rubber-covered, lead, stainless steel, Worthite

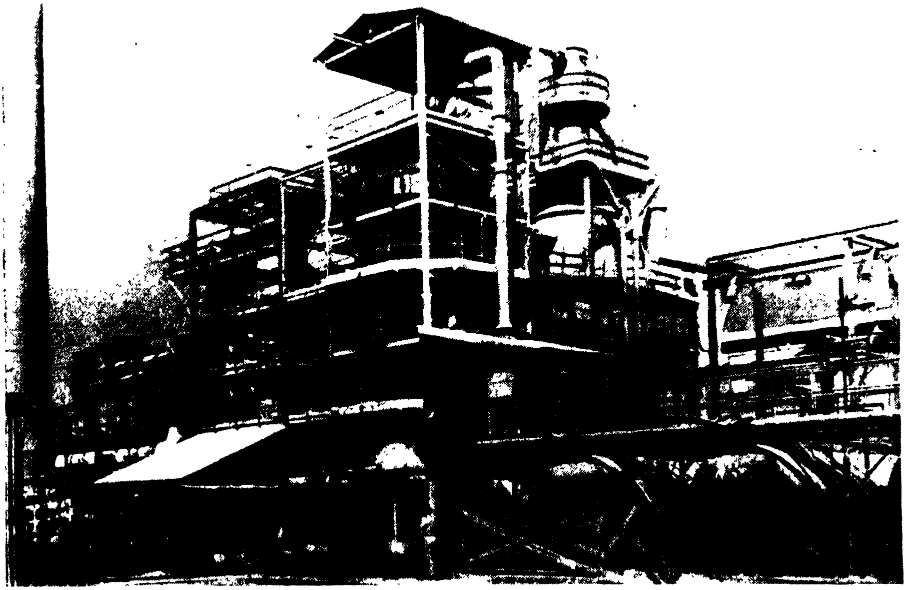
Pipe: lead, lead-lined steel, rubber hose, rubber-lined steel

Exhaust fans: rubber-covered

Fume ducts: rubber-lined steel

In brief, the process is as follows: Phosphate rock is ground either dry or with weak phosphoric acid. It then comes into contact with sulphuric acid. The resulting slurry is agitated continuously in a series of agitators. Rock and acid are added in the exact proportions required by accurate interlocked mechanical feeders. The slurry is cooled during agitation. The acid and gypsum are separated in horizontal-type or table filters. The gypsum goes to waste. The filtrate is strong acid, which is passed over a vacuum filter and goes to storage.

Thermic Process, Electric Furnace.—The concentrated ore from the washing plant and the crushed matrix from the mill are moistened and intimately mixed with finely ground coke or coal before the mixture is carried by belt conveyor to the steel hopper above the moving grate of the sintering machine. Here the fuel in the mixture is ignited by an oil burner or CO gas burner, and as the bed moves forward on the machine, a downdraft causes the balance of the coke or coal to be consumed, thus fusing together all the nonvolatile particles in the mass.



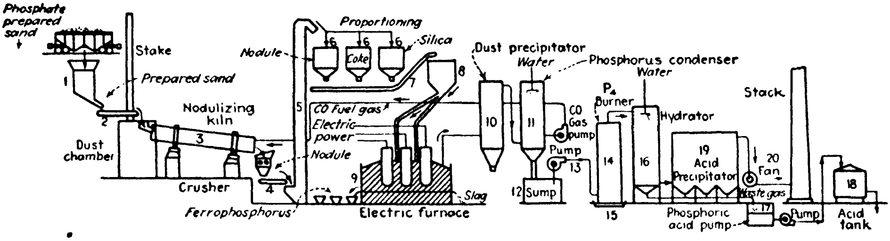
Electric-furnace phosphoric acid plant of Tennessee Valley Authority at Wilson Dam, Ala. Choice of graphite as a material of construction for the new combustion chamber was based on its excellent thermal properties and its resistance to hot oxidizing atmospheres, containing P_2O_5 vapors.

The sintered product drops from the machine to a storage pit, where it is allowed to cool before being ground and sized for furnace use. Fines are returned to the sintering machine, while the coarser product is automatically proportioned with the proper amount of fuel and silica. This is accomplished by three continuous weighing conveyors. From these scales the mixture of sinter, coke, and silica is deposited on a rubber-belt conveyor, which delivers the mixture to stock bins high above the electric furnaces.

The charging of the furnace burden into the furnace is automatic. The carbon electrodes are automatically controlled in relation to electric current.

Phosphorus vapors volatilized from the burners of the furnace are condensed and run into pumps from which the phosphorus is pumped with water to concrete storage tanks.

The newest invention is the graphite combustion chamber for the burning of the liquid phosphorus. It was developed by Tennessee Valley Authority. The chamber is a hollow tower with graphite block wall and base and monolithic cast refractory dome. Blocks are joined by Asplit F cement, a chemical hardening resin cement. It has proved to be effective in resisting attack by the hot P_2O_5 vapor and metaphosphoric acid that in the past resulted in destruction of refractories and refractory cements alike. The chamber base is cupped in a shallow pan constructed of Type 316 stainless steel.



Phosphoric acid (electric-furnace process)

1. Steel
2. Rubber
3. Steel, firebrick-lined
4. Steel
5. Steel
6. Steel
7. Rubber
8. Steel
9. Steel shell, carbon hearth, monolithic cast refractory
10. Steel
11. Steel
12. Steel
13. Bronze case and impeller, stainless steel shaft
14. Graphite wall, monolithic cast refractory dome
15. Type 316 stainless-steel pan
16. Carbon, acidproof brick
17. Acidproof, red shale
18. Wood, lead-lined with red shale brick
19. Carbon tubes in acid brick structure
20. Carbon case, stainless-steel shaft and impeller

The phosphorus feed system consists of phosphorus tanks, a hot-water storage tank, displacement water pumps, interconnecting piping, and a rotameter. The phosphorus feed tanks are filled from the phosphorus condenser sumps of the electric-furnace units or from the phosphorus bulk storage tanks. The gradual build-up of phosphoric acid in the recirculated water is neutralized by addition of soda ash to prevent corrosion of the mild-steel pipe and tanks and the all-iron cocks used throughout the metering system.

The hot gases from the combustion chamber are cooled in a graphite shell and tube cooler located between the combustion chamber and the hydrator. The cooler itself is made up of graphite shell. The gases enter one side of the cooler through a graphite stave duct, pass downward normal to the staggered water-cooled tubes, and pass out the bottom to the hydrator through a carbon-brick-lined steel duct.

Less spray water, above the fixed quantity needed for hydration of P_2O_5, is required for cooling to yield an acid of 82 to 86 per cent H_3PO_4 content collected at 180 to 200°F. (Almond, L. H., and H. K. Steinbiss, Graphite Combustion Chamber for Making Concentrated H_3PO_4, *Chem. Eng.*, Vol. 55, No. 10, pp. 105–109, 1948.)

The impure acid goes to lead-lined tanks, and live steam is blown in until the acid is heated nearly to the boiling point. This dilutes it to 80 to 75 per cent. Sufficient sulphuric acid is added to precipitate the calcium as calcium sulphate and to leave a small amount of SO_3 in solution. This last is quite important, as without this slight excess of sulphuric acid, phosphoric acid of this strength cannot be handled in lead. When a small amount of sulphuric acid is present, a dense scale of lead sulphate, insoluble in phosphoric acid, forms and protects the lead from further attack. After the acid treatment, finely powdered silica is added to combine with the hydrofluoric acid, and then hydrogen sulphide is blown into the acid until it is saturated. The excess silica, suspended matter, and the precipitate of calcium sulphate and arsenic trisulphide are removed by passing the acid through sand filters. (Badger, W. L., and E. M. Baker, "Inorganic Chemical Technology," 2d ed., p. 131, McGraw-Hill Book Company, Inc., New York, 1941.)

Handling

Wood.—For many years wood tanks have been used in phosphoric acid service. In most plants materials have been used as a lining where experience has indicated that the acid is detrimental to the specific species of wood used in the manufacture of the tank.

Where use of wood tanks in phosphoric acid service is concerned, it must be recognized that phosphoric acid effects are intermediate between noncorrosive organic acids and the mineral nonoxidizing acids, such as hydrochloric and sulphuric acids. Phosphoric acid of a given strength hydrolyzes wood more slowly than sulphuric acid of the same strength. A longer life should therefore be expected from a wood tank used to contain phosphoric acid than from a wood tank used to contain sulphuric acid of the same concentration.

There is considerable difference of opinion with respect to the most suitable wood for acid work. Some species have given excellent results in a wide variety of applications of the inorganic acids. Aside from the consideration of oxidizing effect, the pH value of any inorganic acid offers an index of the action on wood of any acid.

Wood is satisfactory for 10 per cent acids. For acid of over 10 per cent strength, a lining has been deemed necessary. A strong acid acts destructively, and a lining of some material is used. Wood tanks have in some instances been in service for 17 years and longer. The wood used was 3-in. fir, and the lining was lead and/or chemical brick. The tanks have not been under pressure but have closed tops. They handled 50 to 75 per cent acid at 75°C.

In the transfer of solutions, wood troughs or launders have an advantage over metals in that wood does not plug and close by scaling. Fume ducts and stacks in phosphoric acid service may be of wood if it is paraffin-treated. In a large chemical plant in the South wood thickeners of the Dorr type have been in use for years on weak acid and have given satisfactory service.

Many manufacturers whose product is from low-grade rock, using sulphuric acid, use tanks and filter presses made of wood. Filter plates are pitch pine, frames are pine or oak, and in one instance the launders or gutters are made of plum-tree wood. Redwood has also been used successfully in phosphoric acid service. (Chaney, S. E., Wood Tanks, *Chem. Eng.*, Vol. 54, No. 2, p. 232, 1947.)

Lead.—Lead is widely used in the commercial production and handling of phosphoric acid because of its satisfactory resistance to this corrosive. For its corrosion resistance lead usually depends upon the low solubility of the thin adherent film of lead compound formed on its surface. Good protection is offered by the lead phosphate film, as it is highly insoluble. Since lead sulphate is also highly insoluble, impure phosphoric acid containing sulphuric acid results in negligible corrosion of lead.

Available data show that lead's resistance to pure phosphoric acid is quite satisfactory and to impure acid is exceptionally good. It is employed with pure acid in concentrations up to 80 per cent at 200°C. and with impure acid up to 85 per cent concentration.

Lead-lined wood or steel tanks have proved very satisfactory for the construction of agitators, thickeners, storage tanks, troughs, and launders. Where sludges are to be handled, an additional lining of acid-resistant brick should be installed to protect the lead from abrasion and from fluorine attack. The majority of failures of lead-lined chemical equipment have occurred as a result of faulty installation or improper design. Where there are temperature changes, sagging of the lead lining is prevented by lead-covered steel straps properly spaced, spacing being dependent upon the temperature differential and other local conditions of design and operation. If the temperature change is excessive, an acid-resistant brick lining will serve the threefold purpose of giving the lead lining additional support without strapping, preventing abrasive action on the lead, and acting as an insulating layer which permits higher temperatures and more rapid temperature changes.

In some types of agitators and thickeners, the raking blades are of hard lead with grains of aloxite embedded in the surface for abrasion resistance. This material is called "plumbalun" and has proved very efficient in resisting combined abrasion and chemical action.

For corrosion resistance, lead pipe and lead-lined steel pipe are used extensively in handling phosphoric acid. The latter is used for operations under pressure and is readily disassembled for ease in removing the crystalline scale, which often forms quite readily. The ease of forming extruded lead pipe into coils has brought about the use of lead steam coils in lead-lined evaporators for concentration of the acid.

Homogeneous lead linings can be used in vacuum evaporators and other installations where a vacuum is applied. Concentration of the acid is also performed in lead vessels employing lead steam coils. (Church, H. M., Lead, *Chem. Eng.*, Vol. 53, No. 9, p. 206, 1946.)

Rubber.—Rubber linings have been extensively used in the manufacture, storage, and distribution of phosphoric acid. In so far as storage and distribution are concerned, the principal problem has been the prevention of product discoloration. Many rubber compounds impart a considerable degree of color to phosphoric acid solutions, but it has been found that relatively pure gum stocks prepared with special control of antioxidants impart little color and result in an entirely satisfactory lining material. Soft-rubber stocks as described above are entirely suitable for handling acid up to 85 per cent concentration and at temperatures up to 150°F.

For process work in connection with preparation of phosphoric acid, higher temperatures are encountered, and where slight obvious discoloration is not objectionable, semihard rubber stocks can be used which permit somewhat higher temperatures, with 180°F. felt to be the safe maximum.

For process work involving extreme high temperatures, it is possible to protect the rubber lining with an inner lining of acidproof brick. In such cases the operating temperature and the temperature gradient through the brick should be controlled so as to limit the maximum temperature at the face of the rubber to approximately 180°F. There are numerous successful installations employing this type of construction.

With regard to the synthetics, these materials have been used commercially for handling phosphoric acid. GR-S is unsuitable for this service owing to the presence of antioxidant used in the preparation of the raw material, which results in excessive discoloration. GR-M compounds have been prepared which compare very favorably with natural rubber in so far as discoloration of product is concerned, and tests indicate that linings of this material should be entirely satisfactory. The GR-M linings carry a preferential price, which has tended to limit the use of the material. GR-I compounds have been prepared which are nondiscoloring and which give satisfactory test results. Preliminary tests with GR-A indicate that satisfactory linings of this material can be developed.

By far the majority of experimental and commercial work in connection with phosphoric acid has been done with natural rubber. Natural-rubber linings have proved entirely satisfactory for the service requirements within the limits specified above and based upon reasonable availability will probably continue to be the standard material used for this service. (True, O. S., Rubber Lining, *Chem. Eng.*, Vol. 53, No. 8, p. 203, 1946.)

Carbon and Graphite.—All the modifications of carbon used structurally in the chemical industry are inert to orthophosphoric acid in all commercial concentrations. These modifications include amorphous carbon, graphite, and impervious carbon and graphite materials. Carbon has been used in electric phosphorus smelting furnaces and phosphoric acid precipitators and ducts for the past 20 to 30 years. It is also used extensively in hydration towers for the absorption of P_2O_5 burner vapors in water.

In none of these applications is there evidence of attack by phosphorus compounds on the carbon, except a slow solution of electric furnace bottoms in unsaturated ferrophosphorus. As a matter of fact, phosphoric acid deposits on carbon protect it from oxidation and permit operation considerably above temperatures (350°C.) normally considered possible when excess air is present.

There is a top temperature limitation of 170°C. on Karbate itself, but by proper equipment design it can be operated in P_2O_5 flue gases without damage. Graphite is now successfully used as the burner chamber for producing P_2O_5. Temperatures are held well below oxidizing temperatures in excess air (450°C.) by external water cooling. There is no evidence of reaction between carbon or graphite and phosphoric acid at any known operating temperature in any of these applications.

Karbate products behave similarly from the chemical standpoint and have been found satisfactory in test and commercial installations in concentrations up to 85 per cent H_3PO_4 at atmospheric boiling point. Major applications of Karbate materials are in acid-conveying systems (pumps, valves, piping), cooling all concentrations of H_3PO_4 in the manufacture of the acid, tubes in vacuum evaporators, and heating solutions typified by those used in the rustproofing of steel. For cooling, cascade coolers and shell and tube heat exchangers are normally used; while for heating, either shell and tube heat exchangers or plate heaters are used.

Contamination of the phosphoric acid by fluorides, sulphates, hydrofluoric and sulphuric acids, such as may be encountered in phosphoric acid production by either the wet or electric-furnace process, has no effect. (Werking, L. C., Carbon, Graphite, *Chem. Eng.*, Vol. 53, No. 9, p. 210, 1946.)

Stainless Steel.—Phosphoric acid is classed as a borderline material with regard to its effect upon stainless steel. That is, in many cases stainless steel can be used with entire satisfaction, but in others serious corrosion difficulties are encountered. The corrosion resistance of stainless steel is believed to be due to the presence of a very thin, continuous, transparent film of oxide which forms naturally when the clean metal is exposed to the atmosphere and which, because of its continuity, prevents further attack on the metal underneath. Any reducing reagent, unless inhibited, will attack this film, while oxidizing agents will cause its renewal should the existing film be abraded or otherwise broken.

Under properly controlled conditions, however, most phosphoric acid products can be handled safely in stainless steel. Difficulties increase, of course, as the concentration increases. Temperature also aggravates the problem, particularly when the material is agitated. Ordinarily, stainless steel should be used only when the temperature does not exceed 200°F.

The fluorides normally present in the phosphate rock represent a major source of trouble in connection with stainless steel. These fluorides must, therefore, be either fully neutralized or eliminated from the phosphoric acid before it can be processed successfully in stainless-steel equipment. This precaution applies to all phases of phosphoric acid manufacture or use, whether it be in baking powder or in fertilizer. Another precaution which must be observed in phosphoric acid manufacture is that filtering agents such as charcoal or diatomaceous earth be confined to the filtering process and equipment. Experience shows that, if even minute particles of such filtering agents pass the filter system, they will tend to settle out on the sides or bottoms of subsequent equipment and through an apparently catalytic action on the oxide film cause corrosion underneath.

This action, as well as other corrosive attack, can be minimized by maintaining stainless-steel surfaces in a scrupulously clean condition. A polish of at least No. 4 finish facilitates cleaning operations. The degree of polish apparently plays an important part in maintaining a more uniform and continuous oxide film on stainless steel, and experience shows that such a surface is most resistant to corrosion attack by phosphoric acid and its products.

Type 316 stainless steel has been found to be most resistant to corrosive attack by phosphoric acid and has been used successfully for storing and manufacturing the chemically pure product as well as certain nonchemically pure grades in which the fluorine content has been controlled. Type 304 stainless has been found satisfactory, when polished, for storing 85 per cent cold phosphoric acid or for handling concentrations up to 5 per cent in various phases of the manufacturing processes. There are occasionally uses where the 321 or 347 stabilized grades can be applied. The ordinary Type 302 should not be used in any phosphoric application.

Good engineering design is essential to the successful use of stainless steel in the phosphoric acid industry. Flanged and dished heads are always to be preferred over flat plate heads, which involve corner or fillet welds. Where rectangular units are necessary, it is preferable to bend the plates so as to bring the welds out away from the corners in order to dress and polish them to best advantage. (Esgar, H. C., Stainless Steel, *Chem. Eng.*, Vol. 53, No. 8, p. 203, 1946.)

Copper Alloys.—Copper and copper-base alloys are used in the form of heat-exchanger tubing, piping, fittings, etc., although the corrosion rates are comparatively high. In the range from room temperature up to 100°C., the corrosion rate of copper-base alloys is comparatively small. However, the corrosion rate at 100°C. is about five times that which takes place at room temperature.

Aeration of phosphoric acid increases the rate of corrosion for copper and its alloys from 10 to 100 fold depending upon the degree of aeration. Since only a limited amount of aeration exists under usual service conditions, it appears that most of the copper-base alloys should be satisfactory for piping and heat exchangers.

The data presented in the literature in connection with water-line corrosion indicate that consideration must be given to this type of corrosion where tubes or pipes are partially immersed in phosphoric acid solutions. Consideration must also be given to the possible increase in corrosion at the water line in partially filled shells of heat exchangers and in tanks.

No definite information is apparently yet available on the effect of velocity on the rate of corrosion of copper alloys in phosphoric acid solutions. Lacking definite information, it would be well to consider the possible corrosion-accelerating effect of impinging or moving streams of phosphoric acid against or on metal surfaces and take precautionary steps. These steps would consist of (1) inserting sleeves at the inlets of tubes in heat exchangers, (2) using heavier elbows and heavier sections adjacent to elbows, and (3) installing deflector or guard plates where the steam enters or leaves a heat exchanger.

Variations in the concentration of phosphoric acid do not have so marked an effect on the rate of corrosion as the concentration of other materials. The impure phosphoric acid produced by the sulphuric acid process may contain a markedly higher concentration of ferric, sulphate, sulphite, chloride, and fluoride ions than the acid produced by the electric furnace process. The presence of these ions increases the rate of corrosion considerably; up to 150-fold increase has been reported as probably being due in the main to the presence of other ions. The life of copper alloys will be very limited when handling phosphoric acid solutions of this type.

Pure phosphoric acid produced by the electric-furnace process contains only small quantities of impurities, such as ferric and fluoride ions, and therefore is generally only slightly corrosive toward copper and its alloys. Yellow-brass piping (Cu, 65; Zn, 35) apparently has been most widely used for handling such solutions.

Accumulation of products of corrosion on metal surfaces may also increase the rate of corrosion and the possibility of pitting. The low-copper alloys, such as yellow brass and naval brass (Cu, 60; Zn, 39; Sn, 1), and other alloys appear to have thin and adherent corrosion films. Copper, copper-silicon alloys, and other high-copper alloys tend to form more voluminous, porous films or scales beneath which roughened or pitted surfaces will be found.

The phosphoric acid vapors in electrostatic precipitators at 95°C. are noticeably more corrosive than pure phosphoric acid solutions at the same or lower temperatures. The rates of corrosion encountered under these conditions are too high for satisfactory service in the form of electrode wire. The high rate of corrosion presumably is due to the abundant supply of oxygen. While the corrosion rate of copper cooling tubes in phosphorus combustion chambers (400 mils per year) is high, the rate is appreciably lower than that characteristic for some other materials. For this reason, the use of copper tubes is feasible for this purpose. (Burlow, C. L., Copper, Copper-Alloys, *Chem. Eng.*, Vol. 53, No. 8, p. 210, 1946.)

Tantalum.—Tantalum is inert to pure phosphoric acid in any concentration at temperatures up to 175°C. However, it is not resistant to the contamination which commonly occurs in phosphoric acid, namely, fluorides.

Where the fluorine concentration is below 10 ppm., tantalum can be used safely and profitably for heat-transfer surfaces in phosphoric acid. Where fluorine concentration is greater, rapid embrittlement will take place, followed by pitting in 2 or 3 months, the rate of embrittlement and pitting being proportional to the fluorine concentration. An appreciable concentration of sulphur trioxide in phosphoric acid is also damaging to tantalum. Where these contaminants are not present, aeration, concentration, or the presence of other impurities such as arsenic have no effect on tantalum.

Tantalum bayonet heaters have been used successfully for heating phosphoric acid of low fluorine content in the processing of the acid to eliminate impurities. Over-all coefficients for heating phosphoric acid with steam range between 600 and 1000 Btu. per sq. ft. per deg. F. per hr., depending upon the temperature and concentration of the acid.

Tantalum heaters are particularly appropriate for the production of food-grade acid, not only because tantalum is insoluble in phosphoric acid but because any particles of tantalum which might get into the acid accidentally would have no detrimental effect in the human body. (Hunter, F. L., Tantalum, *Chem. Eng.*, Vol. 53, No. 8, p. 203, 1946.)

Illium G.—One of the pioneer machinable corrosion-resistant alloys, Illium G, is used extensively by industry and is finding an increasing use in phosphoric acid applications. The alloy was designed to resist that most difficult range of acid corrosion in which both acidic and oxidizing environments are encountered. Both the pure and technical grades of phosphoric acids are resisted by the alloy, and as a general rule corrosion data show that the penetration rates of the alloy in technical acid are slightly higher than in the pure acid. This is owing to the oxidizing action of the impurities usually present in the technical acid. It should be noted that minute variations in the quantity or type of impurities present in the technical-grade acid can greatly change the penetration rates of the alloy.

Illium G is available in casting form and is readily machinable and weldable. It is being used at present in pumps handling phosphoric acid solutions; shaftings, bearings, and impellers for mixing and agitating equipment; liquid metering parts; and a wide variety of miscellaneous applications in the special machinery field. (Johnson, T. E., Illium G, *Chem. Eng.*, Vol. 53, No. 7, p. 221, 1946.)

High-alloy Stainless Steels.—There have been sufficient failures in low-alloy stainless steel to warrant the use of alloys containing greater percentages of, particularly, nickel and molybdenum reinforced with copper. Durimet T and Durimet 20 have fulfilled this requirement. In some of the most severe services, it is anticipated that still higher alloy contents may give a sufficiently longer life to justify the additional cost.

In the manufacture of phosphoric acid from phosphate rock, the fluorine content is of material importance. The phosphate rock in the United States varies in fluorine content from 2.0 to 3.5 per cent. The fluorine content of the phosphoric acid, therefore, is such that in most cases high-silicon iron is not recommended. Durimets T and 20, however, have given excellent service in such processes. The need for this additional corrosion resistance is accentuated by the abrasive action of the gypsum slurries with the phosphoric acid. (Jack, D. E., Durimets T and 20, *Chem. Eng.*, Vol. 53, No. 9, p. 203, 1946.)

Hastelloys.—The Hastelloy alloys, a series of high-strength nickel-base corrosion-resistant alloys designated as grades A, B, C, and D, have excellent corrosion-resistant properties for phosphoric acid. The general rate of attack on these alloys at normal room temperature is higher in the weaker acids, with the corrosion rate falling off rapidly as the strength of the acid increases. In 85 per cent phosphoric acid at room temperature there is practically no measurable rate of penetration. In chemically pure phosphoric acid at room temperatures, the highest rate of attack on any grade is only 0.002 in. per year.

With increase in temperature, the corrosion rates accelerate on Hastelloy A, C, and D, particularly as the strength of the acid increases. Hastelloy B, however, has a relatively low rate of attack in all concentrations. Unlike grades A, C, and D, alloy B has a somewhat lower corrosion rate in boiling 85 per cent acid than it has in the weaker acids. In 85 per cent boiling chemically pure phosphoric acid the rate of attack of 0.00156 in. per year is the same as that encountered in 10 per cent chemically pure acid at room temperature.

It is sometimes more economical to use brass, high-silicon iron, or stainless steel where corrosion rates indicate that a useful life of equipment can be obtained. However, when strength of materials in combination with corrosion-resistant properties is required for critical parts, the Hastelloys can be economically used in spite of their higher initial cost. When freedom from impurities that result from the corrosion product is important, the use of the Hastelloys may be essential. In some cases a useful life might be obtained from equipment fabricated from a material with lower first cost, but the corrosion product would be too great for the requirements of the process.

A large dye manufacturer has used Hastelloys B and C successfully where they must resist phosphoric acid for agitating equipment, blowpipes, and heating coils in glass-lined vessels where it is particularly desirable to avoid contamination in the finished product. Much of this equipment has been in operation successfully for approximately 6 years. Many of the large phosphate plants are employing Hastelloy B successfully in the form of agitators, mixing paddles, thermometer wells, piping, pumps, and valves. Hastelloy B is generally the most resistant to phosphoric acid, with alloy C next. Since both grades are available in the form of castings, hot-rolled sheet, plate bar stock, welding rod, welded tubing, and drawn wire, they can be used successfully as materials of construction for practically any type of equipment required to process phosphoric acid. (Chisholm, C. G., Hastelloy Alloys, *Chem. Eng.*, Vol. 53, No. 7, p. 222, 1946.)

Glass-lined Steel.—The question frequently arises regarding the chemical durability of glasses, as applied to steel equipment, toward the action of various concentrations of phosphoric acid at room and elevated temperatures. The present-day status of the corrosion-resisting property of glasses for handling phosphoric acid may be briefly stated as follows:

1. Glass-lined steel equipment should not be considered for handling phosphoric acid containing even traces of soluble fluorides, either at room or elevated temperatures, due to the fact that the impure acid will attack the glass, resulting in marked disintegration of the glass lining. The rate of attack is accelerated as the temperature increases.

2. Glass-lined steel equipment may be successfully used for handling phosphoric acid, free from soluble fluorides, at temperatures not greatly in excess of room temperature.

3. Glass-lined steel equipment is not recommended for handling high concentrations of phosphoric acid free from soluble fluorides at elevated temperatures because of a gradual disintegration of the glass, with the result that the service life of the equipment may be unsatisfactory. (Chormann, O. I., Glass-lined Steel, *Chem. Eng.*, Vol. 53, No. 7, p. 226, 1946.)

Vinyls.—In the heavy-chemical industry, the vinyls can be used wherever phosphoric acid in any concentration is processed. They have a definite application in the manufacture of phosphoric acid by the strong-acid process, the electric-furnace process, or the blast process. Equipment suitable for protection with vinyl linings includes spray tanks, purification and slurry tanks, wash tanks, filters, storage tanks, mixers, and absorption towers. Wherever elevated temperatures are encountered, brick sheathings should always be considered as a margin of safety.

In the metal-finishing industry, wherever phosphoric acid is used in cleaners or in metal preparation, the equipment may be completely protected by the use of vinyl linings.

In organic synthesis and processes involving organic chemicals and phosphoric acid, caution must be exercised in the use of vinyl linings because of the by-products formed, which may exert a solvating effect on the lining. Solvents such as ketones, esters, chlorinated hydrocarbons, and aromatic hydrocarbons tend to swell or dissolve vinyl linings. Processes involving phosphoric acid and alcohols, ethers, and aliphatic hydrocarbons can be handled safely. The above information applies equally to the salts of phosphoric acid in any concentrations, again the services being subject to the maximum temperature limitation.

In some cases, vinyl-base paint can be used to protect equipment from phosphoric acid, wherever temperatures are not encountered. It is not recommended that paints be used to build up a lining on the interior of a processing tank wherever agitation or temperature is encountered. In dilute acid and normal temperatures, a built-up coating of six to eight coats will serve for mixing, storage, or shipping. The paint can be applied to new porous wood tanks or to properly constructed concrete storage tanks. (Siddall, D. F., Vinyl Plastics, Paint, *Chem. Eng.*, Vol. 53, No. 8, p. 206, 1946.)

Chemical Stoneware.—This material, in common with other compounds containing silica, reacts to some extent with phosphoric acid. This reaction is negligible at ambient temperatures, and therefore chemical-stoneware equipment is suitable for use with phosphoric acid under these conditions. In fact, it may be stated that under ordinary industrial conditions the action of phosphoric acid on silica is not sufficiently great to render its use inadmissible owing to the fact that reaction occurs at temperatures greater than those at which chemical stoneware is commonly used.

Experience has shown that temperatures greater than 80°C. should not be employed, although a search of the literature indicates that severe deterioration does not occur under 150°C. If the temperature limitation is adhered to, any concentration can be used.

Generally speaking, it is only in the handling operations such as pumping, storage, and mixing that chemical stoneware is used. Typical equipment for this purpose are chemical-stoneware pumps, cylindrical vessels, rectangular tanks, and both conical flange and bell-and-spigot piping. (Herstein, F. E., Chemical Stoneware, *Chem. Eng.*, Vol. 53, No. 8, p. 208, 1946.)

Nickel Alloys.—Use of nickel and the nickel alloys, Monel, Inconel, and Ni-Resist, with phosphoric acid is generally limited to the relatively pure acid derived from phosphorus vaporization processes (blast or electric furnace). Crude phosphoric acid produced by the treatment of phosphate rock with sulphuric acid usually contains ferric salts in an amount sufficient to make the solution highly oxidizing and consequently corrosive to these materials under most conditions.

Monel has useful resistance to unaerated pure phosphoric acid solutions of all concentrations at temperatures up to about 220°F. At higher temperatures corrosion is usually appreciable, although there is some indication that, in very strong acid such as tetraphosphoric containing 85 per cent P_2O_5, resistance is adequate up to 350°F. In phosphoric acid solutions, corrosion of Monel is usually increased considerably by a high degree of aeration, particularly in the concentration range of about 10 to 50 per cent H_3PO_4.

Nickel and Inconel are resistant to phosphoric acid solutions of all concentrations at atmospheric temperature. Their corrosion rates are increased somewhat by a high degree of aeration. Hot concentrated solutions of the pure acid are very corrosive to both nickel and Inconel. Inconel, because of its chromium content, will frequently have useful resistance to crude phosphoric acid solutions at temperatures close to atmospheric, but not at more elevated temperatures. (Friend, W. Z., Nickel, Nickel Alloys, *Chem. Eng.*, Vol. 53, No. 9, p. 203, 1946.)

Haveg.—Haveg 41, in which the plastic component is of the phenol-formaldehyde type, has been used in phosphoric acid service with good results. In the past, however, there have been limitations with regard to both temperature and concentration. As the result of improvements in the 41 resin the range of successful operation has been greatly extended.

In testing Haveg material, two strengths of phosphoric acid were employed. Concentrated phosphoric at 1.71 sp. gr. (over 85 per cent H_3PO_4) was used in one test, and acid of 50 per cent strength in another. In the case of the weaker acid, tests were made on submerged samples at temperatures of 25, 50, and 100°C. In the case of the concentrated acid, the tests were conducted at the temperatures stated and in addition at 150°C. The time intervals varied from 80 to 93 days' submergence. Samples at the end of the test were evaluated on the basis of weight change, volume change, appearance of sample, and appearance of solution. The individual observations were weighted according to a system which experience has indicated coordinates well with actual field results.

The earlier Haveg under the conditions stated rated in the case of the 50 per cent acid as excellent at 25 and 50°C. but unsuitable at 100°C. In the case of the concentrated phosphoric, the earlier material rated good at 25, fair at 50, but unsuitable at 100 and 150°C.

For the improved and presently used type Haveg, the results with the 50 per cent acid were excellent at 25, 50, and 100°C. In the concentrated acid the newer Haveg was rated excellent at 25, 50, and 100°C. and good at 150°C.

By relationship of service performance of the older grade with the test performance of the newer grade it would seem that the present type Haveg 41 offers an excellent material to be employed in many types of equipment where resistance to corrosion by phosphoric acid is a factor. (McWhorter, P. L., Jr., *Chem. Eng.*, Vol. 53, No. 9, p. 208, 1946.)

High-silicon Iron.—Silicon iron cannot be recommended for use on hydrofluoric acid or other compounds of fluorine. Thus the success of using it on phosphoric acid depends entirely on whether the acid is pure or in the crude form, the latter invariably involving compounds of fluorine either as hydrofluoric acid or as silicon fluoride. This condition will hold regardless of concentration or temperature of the crude acid.

Much work was done in the 20's on new processes and types of equipment in the manufacture of phosphoric acid, both the so-called dry method using elemental phosphorus and the wet method using sulphuric acid. Silicon iron was used widely on both because of its known resistance to phosphoric acid and because its extreme hardness gave excellent resistance to abrasion and erosion in the wet method. Though it was known that the presence of fluorine in the latter might have a marked effect on its life, at least one operator reported that excellent service was derived "even though not recommended by the manufacturer." Much of the original silicon iron remains in service on pure phosphoric acid, and in many cases it continues to be used on the crude in spite of its shorter life. Continued use seems justified because of its high resistance to abrasion. (Shields, R. M., High-Silicon Iron, *Chem. Eng.*, Vol. 53, No. 9, p. 212, 1946.)

Vitreous Silica.—Reaction between vitreous silica and phosphoric acid is inappreciable at temperatures below 200°C. but increases rather rapidly at higher temperatures.

Vitreous silica is readily attacked by fluorine compounds at high temperatures but is unaffected by sulphur trioxide or oxidizing conditions. Mixtures of concentrated sulphuric and phosphoric acids can be distilled in vitreous-silica equipment with only very small resultant attack.

Vitreous-silica cascade concentration trays, dishes, and coolers, similar to those used as sulphuric acid units, have given excellent service in concentrating pure phosphoric acid to U.S.P. strength at operating temperatures of 200 to 230°C. with an occasional maximum of 260°C. Closed-end tubes of the same material were used in this connection for thermometer and pyrometer wells. The dishes on the lower steps, handling the strongest acid at highest temperatures, have rather a short life, but the service given exceeds that with glass or porcelain by a considerable margin.

Electric immersion heaters in vitreous-silica envelopes are especially adapted to heating phosphoric acid solutions in vessels of any other material where purity of product is vital. (Winship, W. W., Vitreous Silica, *Chem. Eng.*, Vol. 53, No. 9, p. 214, 1946.)

PHOSPHATES—SULPHURIC ACID

Carbon, graphite, and Karbate materials have proved satisfactory for service with mixtures of sulphuric acid and phosphates. (Palmquist, W. W., Carbon and Graphite, *Chem. Eng.*, Vol. 55, No. 6, p. 236, 1948.)

PHOSPHORIC ANHYDRIDE

Phosphoric anhydride is not of itself corrosive, but with water it forms phosphoric acid, which is very corrosive.

Packaging

Wooden barrels, kegs, or boxes are used, with inside containers which must be tightly stoppered glass bottles or metal cans. Metal barrels or drums are also used. (Manufacturing Chemists Association, "Phosphoric Anhydride," Chemical Safety Data Sheet SD-28, 1948.)

PHOSPHORUS

Phosphorus is not corrosive in the absence of air and water, but some trouble occurs when moisture is present.

Production

See Phosphoric Acid, page 266.

Handling

Phosphorus is stored under water. Since it is slightly soluble in water, certain gaseous compounds are formed, and minute particles detach themselves from the main body of the phosphorus, which oxidizes in the cover water and slowly acidifies it. (Manufacturing Chemists Association, "Phosphorus, Elemental," Chemical Safety Data Sheet SD-16, 1947.) The temperature of the cover water is a factor in the acidification. As high temperatures are reached, the solubility of the phosphorus increases, causing a more rapid acidification. This process will in time corrode the container at the liquid-level line. When the acidity is in excess of 0.5 per cent, the cover water should be neutralized with lime or soda ash.

Storage tanks may be constructed of concrete or welded steel without bottom or side outlets. They should be placed in retaining basins, also constructed of concrete or welded steel.

To avoid corrosion at the water line, internal coils and all pipe lines should be equipped with noncorrosive sections at those points where the pipes enter the liquid.

Plug or gate valves (all-steel) are preferable to other types.

Packaging

Phosphorus may be shipped in steel tank cars, drums, or cans.

PHOSPHORUS OXYCHLORIDE

Production

Materials of Construction.—Phosphorus oxychloride is corrosive to most common construction materials. Storage tanks may be constructed of lead or homogeneous lead-lined steel or nickel or nickel-clad steel of welded construction. Other materials suitable for storage tanks are ceramic ware, glass, and glass-lined steel. Storage tanks should be vented or equipped with frangible disks made of nickel or lead and designed to release at a predetermined pressure. (Manufacturing Chemists Association, Manual Sheet SD-26, p. 6, 1948.)

Pipe lines should be sloped to the outlet to provide maximum drainage. Piping preferably should be of lead or nickel. Piping made of stainless steel, glass, or suitable plastic material also can be used. (*Ibid.*)

Chlorimet 2 valves are used on this service for extreme purity.

Nickel equipment for the production of phosphorus chloride compounds has been adopted by some producers where strength plus corrosion resistance are essential. It is variously used for reactors, coolers, piping, and valves, performing especially well in the complete absence of water.

Lead also provides good resistance and is often used for nonstressed parts such as coils and receivers.

A fibrous form of Teflon has been developed that can be molded with a small percentage of binder to yield a packing ring suitable for high-speed pumps. Since the amount of binder required rarely exceeds 7 per cent, the chemical resistance of the packing ring is excellent. These packings have been used with excellent results on pumps handling phosphorus oxychloride.

Packaging

Phosphorus oxychloride is classified by the I.C.C. as a corrosive liquid. As such it must be packed in I.C.C.-specification containers when shipped. These are as follows: wooden boxes with glass or earthenware inside containers, wooden barrels or kegs with glass or earthenware inside containers not over 2 gal. each (the glass or earthenware containers must be cushioned in the outside containers by means of incombustible elastic packing material), metal-jacketed lead carboys, lead-lined metal barrels or drums.

It can also be shipped in nickel drums. Tank cars can be used when the tanks of these cars are lead-lined or made of solid nickel at least 99 per cent pure and when all cast-metal parts of the tank in contact with the lading have a minimum nickel content of 96.7 per cent. Tank motor vehicles with tanks that are lead-lined can be used.

PHOSPHORUS TRICHLORIDE

Phosphorus trichloride is corrosive to most common construction materials. By contact with moisture, hydrochloric and phosphorus acids are formed which are extremely corrosive.

Handling

Nickel, lead, and ceramic ware are suitable materials for construction of storage vessels. Glass-lined tanks can also be used. Of all these, ceramic ware is the least desirable for phosphorus trichloride storage tanks because it is frangible and vessels constructed of it are difficult to keep tight. (Manufacturing Chemists Association, Chemical Safety Data Sheet SD-27.)

Lead-lined steel tanks are satisfactory (nickel or nickel-lined tanks can be used). It is suggested that frequently used outlets be fitted with a gate valve and a lead cover or shield over the open end of the line if such an open end exists. (*Ibid.*)

Packaging

This chemical can be shipped in wooden barrels or kegs with glass or earthenware inside containers. Metal-jacketed lead carboys, lead-lined metal barrels or drums, or nickel drums are other containers in use.

Phosphorus trichloride can also be shipped in tank cars when the tanks of the cars are lead-lined or made of solid nickel at least 99 per cent pure and when all cast-metal parts of the tank in contact with the trichloride have a minimum nickel content of 96.7 per cent.

Tank motor vehicles can be used when tanks are lead-lined. (*Ibid.*)

PHTHALIC ANHYDRIDE

There are several processes in use for the production of phthalic anhydride. Gibbs and Conover discovered the process consisting of a controlled catalytic air oxidation of naphthalene. Oxidation of naphthalene to phthalic anhydride with the aid of fluid catalyst was developed by Sherwin-Williams Co. It was first made from petroleum raw materials by Oronite Chemical Co.

Production

Materials of Construction.—Plain cast iron and steel are used for much of the equipment. The reactor and converter tubes are steel; in fact no stainless steel or other special materials are used in the fluid-catalyst plant. (Lee, J. A., Fluid Catalysts Make Their Debut in Chemical Production, *Chem. & Met. Eng.*, Vol. 52, No. 7, pp. 100–101, 1945.) In the petroleum process molten anhydride is stored in aluminum. (Callaham, J. R., Phthalic Anhydride from Petroleum Breaks a Coal-Tar Tradition, *Chem. Eng.*, Vol. 53, No. 8, pp. 116–119, 1946.) The chilling machine is stainless steel.

Fluid-catalyst Process.—The process consists of passing heated air and molten naphthalene which is vaporized by direct contact with the catalyst charge up through a steel reactor. The naphthalene is converted to phthalic anhydride.

Reaction-product gases after leaving the dense catalyst phase pass through a settling zone into an internal cyclone system, where most of the catalyst is removed from the vapors. The vapors then pass through a steel cooler. From this heat exchanger the vapors pass through a catalyst recovery system. The system consists of specially designed filters.

The filtered product gases are passed to a phthalic anhydride recovery system which separates anhydride from tail gases. Molten anhydride is transferred to a receiver and then is pumped by a steel submerged centrifugal pump to a feed tank. It goes to a flaker.

Petroleum Process.—The process consists of (1) feeding preheated air and vaporized *o*-xylene into catalyst-filled tubes, where conversion to phthalic anhydride takes place; (2) cooling the resulting vapors in heat exchangers; (3) condensing and removing the crystals of anhydride; (4) melting the crystals and distilling for purification; (5) solidifying the phthalic anhydride into physical form for market.

The primary still is direct fired and equipped with steel conventional-design packed columns. Molten anhydride product is pumped to an aluminum storage tank blanketed with inert gas and heated by means of internal steam coils. From here it is fed to a stainless-steel water-cooled surface for solidification.

Handling

Phthalic anhydride can be handled in ordinary materials of construction. Molten phthalic anhydride is stored in aluminum tanks. Aluminum reaction vessels are used to prepare water-white plastics, of which this chemical is an ingredient.

Packaging

It is shipped in paper bags but could be transported or packaged in almost any type of container.

PICKLES

The salting and curing of pickles is done in wooden tanks. (Wormley, W. G., 40 Years of Pickle Salting, *Food Ind.*, Vol. 11, No. 9, pp. 486–488, 1939.) The tanks can be made of cypress, fir, pine, or redwood, with tapered or straight sides. The cypress tank, though the most expensive, is the best under all conditions, especially if the tank is erected in the open, as cypress does not dry out so quickly as other woods. Fir is much cheaper and will be very efficient under cover if the tank is kept full at all times, but it must never be permitted to stand empty for any length of time, for fir dries out very quickly, soon causing the tank to leak. And thereafter it is very hard to keep tight.

There are many redwood pickle tanks that have been in service for over 20 years. Some have seen over a third of a century of service. (California Redwood Association, *Tech. Bull.* 16–5.)

Each tank should be supplied with a wooden pump. Where electric power is not obtainable or where labor is cheap, the common iron pitcher pump with 1½-in. galvanized-iron pipe and check valve is used, but in most places the electrically driven rotary pump is used. One firm is using a pump consisting of a pump log, a stainless-steel propeller, and a small electric motor. Power consumption is very low. (Wormley, *loc. cit.*)

The handling and processing of highly acid and corrosive products, such as brines and other mixtures containing vinegar and salt, have always presented difficulties. (Mitchell, W. M., Steel Alloys, *Food Ind.*, Vol. 7, No. 12, pp. 577–579, 1935.) There are few metals that will successfully withstand the vinegar-salt combination in pickles. Notwithstanding the corrosive nature of these combinations, they are successfully handled with 18-8 stainless steel, but on account of the unusually corrosive nature, precautions must be observed to wash and rinse all equipment thoroughly after use; otherwise pitting may eventually occur.

In processing pickles, a 10 to 15 per cent brine solution at 70 to 100°F. is recirculated by means of a high-silicon iron pump. Valves, pipe, and fittings of the same alloy are also used.

PICKLING SOLUTIONS

The pickling of metals is a large and important field. Many such metals as stainless steel, carbon steel, and brass are treated and many chemicals are used in the pickling solutions. Among them are nitric acid, sulphuric acid, hydrofluoric acid, acetic acid, and caustic soda. It is no wonder that a variety of metallic and nonmetallic materials of construction is used for the pickling tanks and accessories.

Handling

Sulphuric Acid.—Rubber-lined tanks have been extensively used in connection with sulphuric acid. Rubber linings are usually protected with inner linings of acidproof brick or cement, usually provided to protect the rubber against mechanical abuse.

In the steel industry, practically all the large tanks used for the pickling of wide strip steel are protected with acidproof linings constructed of brick jointed with sulphur cement. (Payne, C. R., and W. W. Duecker, Chemical Resistance of Sulphur Cements, *Trans. A.I.Ch.E.*, Vol. 36, pp. 91–111, 1940.) The continuous-pickling units containing 8 to 15 per cent sulphuric acid are 300 ft. long. Since the construction of the first of the tanks, skid blocks have been designed which are cemented directly into the sulphur-cement lining and thus prevent excessive abrasion on the lining. The acid bath is operated at 80 to 90°C. Numerous other tanks constructed with the aid of sulphur cement, such as batch-pickling tanks, tanks for the pickling of billets and rods using various types of mechanical devices, have been in service for many years. Tanks, floors, and sewers used for the collection, neutralization, and disposal of the waste pickling solution are usually lined with sulphur-cement jointed brickwork.

Durimet 20 and high-silicon iron equipment are giving satisfactory service in sulphuric acid pickling solutions of 6 to 10 per cent acid at 180°F. in batch pickling and 25 to 30 per cent at 220 to 230°F., in continuous picklers, provided high temperatures are not involved. (From W. A. Luce of the Duriron Co.)

High-silicon iron finds particular applications in such items as dancer rolls and guide rolls, where good mechanical properties and good corrosion resistance are required. Other equipment used in this type service are pumps, tank outlets, jets, valves, rocks, and skid bars. High-silicon iron pumps are also being used to circulate sulphuric acid countercurrent to the strip in semicontinuous strip picklers.

Pickling crates of Monel and Monel tie rods for pickling tanks are used in hot sulphuric acid solution. Monel has been found to be serviceable for structural parts of scrubbers for steel sheets after pickling. They must stand dilute sulphuric acid solution.

Hastelloys C and D are used to handle the normal 10 per cent sulphuric acid pickling solution at a temperature of 180°F.

Glass tanks have been used for pickling solutions of 50 per cent sulphuric acid at 220°F.

Of the copper alloys, the silicon, aluminum, and leaded bronzes are usually favored where sulphuric acid is to be handled as in the pickling of steel. (La Que, F. L., *Can. Chem. Process Ind.*, p. 185, May, 1938.)

Where brass-pickling solutions have copper sulphate added to the sulphuric acid batch, tanks, conveyors, and pumps of 304 or 316 stainless steel have frequently been used. The copper sulphate acts as an inhibitor on the stainless steel.

Nitric Acid–Hydrofluoric Acid.—Carbon bricks are frequently used as construction for tank linings in the pickling of stainless steel in solutions generally ranging from 10 to 14 per cent nitric acid with 2 to 4 per cent hydrofluoric acid. (Gaylord, W. M., Carbon and Graphite, *Chem. Eng.*, Vol. 55, No. 3, p. 225, 1948.) Such linings have been in service many years with no apparent evidence of brick deterioration. Karbate-plate heat exchangers have been in service in stainless-steel-pickling operation for several years with practically no maintenance.

Sulphur cement containing carbon as a filler is the only jointing compound that will withstand this combination of acids. (Payne and Duecker, *loc. cit.*)

Mixtures of nitric and hydrofluoric acids used in cleaning stainless steel have no effect on Koroseal. (Schoenfeld, F. K., Koroseal as an Engineering Material, *Trans. A.I.Ch.E.*, Vol. 35, pp. 447–462, 1939.)

Durimet steam jets are used in steel mills in the electrolytic pickling of stainless-steel strip. The solution is 20 per cent nitric acid and 3 to 5 per cent hydrofluoric acid. (Luce, W. A., Durimet and Chlorimet, *Chem. Eng.*, Vol. 55, No. 2, p. 233, 1948.)

Nitric Acid.—Inconel commonly is used for baskets and other parts in the pickling of brass parts in cold nitric acid solutions. (Friend, W. Z., Nickel, Nickel Alloys, *Chem. Eng.*, Vol. 55, No. 4, p. 219, 1948.)

Glass tanks are in use for handling a nitric acid pickling solution of 42°Bé. at 120°F. and also for handling one of 14 per cent nitric acid and 8 per cent sodium bichromate at 100°F.

Hydrofluoric Acid.—Monel is used for holding a hydrofluoric acid pickling solution for cast iron.

Acetic Acid.—High-alloy stainless steels such as Durimet or Worthite (pumps) have been used for handling 15 per cent acetic acid at 100°F. in magnesium-sheet pickling.

Aqua Regia.—Pyroflex with a fused-on ceramic lining the steel outer shell is used for pickling tanks for cleaning brass. Strong nitric, sulphuric, and muriatic acids are used for producing aqua regia. The tanks operate at temperatures up to 180°F. (Rauh, C. A., Pyroflex Constructions for Acid and Alkali Service, *Trans. A.I.Ch.E.*, Vol. 35, pp. 463–472, 1939.)

Caustic.—Inconel is being used for heaters for molten-caustic pickling baths at about 900°F.

Sulphuric Acid–Hydrochloric Acid.—Haveg is extensively used in the form of cylindrical and rectangular tanks, fume systems, pumps, and piping for copper and steel pickling where acid concentrations of 5 to 20 per cent are commonly employed. Its scope in such applications is broadened by its excellent resistance to sulphuric pickling solutions containing other agents such as hydrochloric acid or ferric sulphate.

Hydrochloric Acid.—Tantalum U heaters are in service heating HCl in brick-lined pickling tanks.

Phenolic laminated hold-down rolls are used. Carbon is used also for hold-down rolls in continuous alternating-current pickling machines.

Lead-covered rods are used in pickling tanks.

Tantalum heaters are reported being used in tanks used for pickling tin-plate steel products prior to hot-dip tinning.

Light pickling tanks are frequently made of cypress, and the heavier tanks of longleaf yellow pine.

Monel is used for crates, racks, baskets, chains, hooks, and other parts holding the steel to be pickled; for bolts, nuts, stay rods, and other parts supporting wooden pickling tanks; and often for the tanks themselves. (International Nickel Co., *Bull.* T-3, 1939.)

Monel has performed quite satisfactorily when used for hoods enclosing continuous pickling tanks. The atmosphere of hydrogen within such hoods favors the good performance of Monel.

Saran-lined steel pipe is used for a 2-in. blower line to a chrome-pickle bath.

Acid pickling vats are sometimes protected by a coating of phenolic resin.

Worthite and Durimet are being used to handle pickling acids.

POLYETHYLENE TEREPHTHALATE

The development of a process for the production of the fiber-forming polyester, polyethylene terephthalate, has been described. The polyester is obtained from ethylene glycol and methyl terephthalate by ester interchange. (Hardy, D. V. N., Polystyrene Terephthalate and Its Early Development, *J. Soc. Chem Ind.*, Vol. **67**, No. 11, pp. 426–432, 1948.)

Production

Materials of Construction.—All parts of the equipment in contact with the polyester should be made of stainless steel, and their surfaces should be highly polished. When cold, the polyester readily separates from polished stainless steel.

Process.—To prepare the terephthalic acid, *p*-cymene is oxidized with nitric acid and the product further oxidized with potassium permanganate to terephthalate acid. This is esterified, then purified by vacuum distillation and subsequent crystallization. The condensation of glycol and methyl terephthalate is carried out in stainless steel.

POLYGLYCEROL

The low-viscosity material is made by heating 4.5 tons of glycerol with 12 kg. of caustic soda in a stainless-steel kettle at 250°C. for 6 to 8 hr. The loss of water is 11 to 12 per cent, and the yield 4 tons. The viscosity of a 90 per cent aqueous solution should be 150 sec. in a No. 4 Ford cup at 20°C.

The high-viscosity material is made by heating at 260°C. for 10 to 12 hr., the loss in weight being 22 to 24 per cent; the viscosity of a 75 per cent aqueous solution is 40 to 50 sec. in a No. 2 Ford cup at 20°C. This brand is used in the manufacture of Soromins (textile auxiliary products). (Adams, D. A. W., and W. Baird, Some Miscellaneous Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.)

POLYISOBUTYLENE

The German I.G. Farben. plant at Oppau was visited by an American team of chemical engineers in 1945 to obtain information on the production of polyisobutylene. [Boundy, R. H., and R. L. Hasche, Manufacturing of Thermoplastics in Plants of I.G. Farben., Report' 1069, Combined Intelligence Objectives Committee, G-2 Division, SHAEF (Rear) APO 413, U.S. Department of Commerce.]

Production

Materials of Construction.—Each polymerization unit was made up of a horizontal endless stainless-steel belt 12 in. wide by 20 ft. long (running length). The top side of the belt was held cup shape by idlers. Thus, the belt acted as the continuously moving container for the polymerizing mixture. The belt moved 2 ft. per sec. It was housed in a cylindrical steel shell.

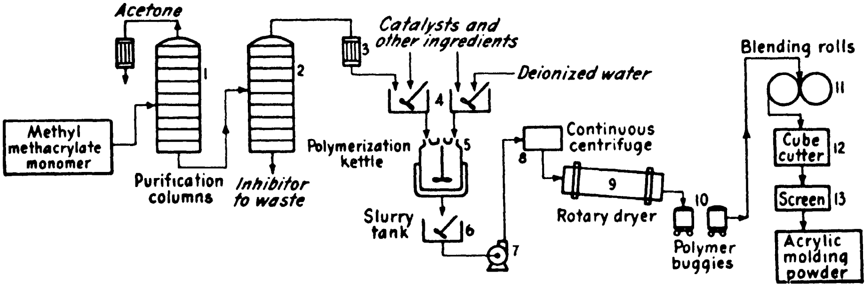
Process.—Polymerization was at atmospheric pressure, and the housing was only gastight. The ethylene with dissolved catalyst, boron trifluoride, was mixed with the isobutylene just as it poured onto the belt. Polymerization was practically complete in the first 6 ft. of belt travel. Vaporized ethylene passed to a gas holder, then was compressed, condensed, and recycled. The polymer was spongy because of ethylene vaporization and completely filled the belt. The polyisobutylene was scraped from the belt at the extreme end of its travel and fell into a hopper of a double-screw extruder, where it was milled and extruded into sheets. The extruder was of iron and steel construction.

POLYMETHYL METHACRYLATE

Polymethyl methacrylate, a plastic known as Lucite, is produced by the E. I. du Pont de Nemours & Co. at its Washington, W.Va., works.

Production

Materials of Construction.—Few of the materials used in this plant are by their nature corrosive. The materials of construction problem was not one of prevention of corrosion but rather one of maintaining purity and clarity of the product. Hence all equipment which touches the product in any way is made of stainless steel, most of it Type 347. (Williams, Roger, Jr., How Washington Works, *Chem. Eng.*, Vol. 55, No. 9, pp. 118–121, 1948.)



Acrylic molding powder. All stainless steel.

Process.—Polymethyl methacrylate production begins with receipt of methyl methacrylate monomers in tank cars from the company's plant at Belle, W.Va. The monomer, which has been inhibited against polymerization, must first have the inhibitor removed. This is done in a two-step distillation. In the first still, the monomer is the tails and any impurities left, such as acetone, are taken off overhead. In the second still, the monomer is distilled over, leaving the inhibitor and any high-boiling impurities in the tails product. The pure monomer then goes to a hold-up tank for feeding to the polymerization system.

The polymerization unit is completely automatic in operation. Typical of all the plant's operations, all the operator has to do is push a button to start the cycle going. Once in motion, the several ingredients are automatically measured out into dissolving tanks, and the dissolving tanks are then emptied into the polymerization kettle.

The polymerization vessel is a jacketed, stainless kettle which is agitated with an anchor-type agitator. The first part of the cycle consists in heating the charge to polymerization temperature by injecting steam into the jacket. Then when reaction begins, water is admitted to the jacket to remove heat of reaction and give a constant-temperature polymerization. At the end of the cycle, the emulsion of polymer and water is cooled to stop reaction and is dropped by gravity into a slurry tank below the polymerization kettle. Note that up to this point all materials movement in the polymerization system has been by gravity.

Slurry of polymer particles in water is next pumped to a continuous Bird centrifuge. The wet solids from the centrifuge feed into a rotary dryer made of highly polished stainless steel. This polish is necessary for cleaning when changing from one formula polymer to another. Finished polymer from the dryer drops into a polymer "buggy." This is a small vessel mounted on detachable legs which can be moved around the plant by means of hoist trucks.

The buggies fulfill another function—they are also blenders. Many Lucite formulations require additives and, of course, color in many cases. Additives are put into the buggy, which is then placed on a set of rolls and turned over and over until the ingredients are completely blended. The buggy is then moved directly over the hopper that feeds the polymer milling rolls.

Milling of the polymer is set up to require minimum attention by operators. At the end of the milling, the polymer is fed through cooling baths and a cube cutter. From the cube cutter the product falls directly into the fiber-drum shipping container.

POLYSTYRENE

The Ludwigshafen plant of the I.G. Farben. was visited in June, 1945, to obtain information on the manufacture of plastics and plastic intermediates. [Boundy, R. H., and R. L. Hasche, Manufacturing of Thermoplastics in Plants of I.G. Farben., Report 1069, Combined Intelligence Objectives Committee, G-2 Division, SHAEF (Rear) APO 413, U.S. Department of Commerce.] A number of grades of polystyrene were produced at this plant.

·Production

Materials of Construction.—Stainless-steel and glass-lined equipment were used extensively for the important pieces of equipment.

Emulsion Polymerization.—Monomeric styrene 99.5 or, better, pure was employed in a ratio of 30 to 35 per cent styrene and 65 to 70 per cent water. Catalyst was 0.1 per cent potassium persulphate and 1 per cent of an emulsifying agent. Polymerization was carried out in glass-lined or stainless-steel jacketed and agitated kettles. Temperature at the start was 70°C. and increased to 95°C. in 4 hr., when polymerization was complete. Drying was accomplished by flashing off all water and the residual monomer. This was done in a set of stainless-steel rolls which were heated by steam at 160°C.

Mass Polymerization.—Massive polymerization of styrene was carried out continuously in a water-jacketed tower of stainless steel. It was divided into six sections, the lower five of which contained coils for heating and cooling. The upper five sections were jacketed, and the bottom section provided with an external electrical heating unit.

In operation the tower was filled with styrene to the top and temperature maintained at 180°C. at the bottom and 120° at the top. Polymerization required 24 hr. After polymerization was completed, styrene was added at the top and discharged from the bottom through a screw and thence through twin orifices onto a stainless-steel sheet belt conveyor. At the end of the conveyor, it was cut into short lengths with a rotating cutter and then ground in a mill.

POLYVINYL CHLORIDE

The I.G. Farben. made polyvinyl chloride at Bitterfeld and Schkopau. The former plant used a batch method, and the latter continuous. [Boundy, R. H., and R. L. Hasche, Manufacturing of Thermoplastics at Plants of I.G. Farben., Report 1069, Combined Intelligence Objectives Committee, G-2 Division, SHAEF (Rear) APO 413, U.S. Department of Commerce.]

Production

Materials of Construction at Bitterfeld.—The vinyl chloride was stored and handled up to the reactor in ordinary iron equipment. Some of the reactors were nickel, and some were glass-lined steel. The spray dryers were iron. The polyvinyl chloride was stored in iron.

Materials of Construction at Schkopau.—The reactors in this plant were jacketed, vertical glass-lined cylinders with a paddle agitator. As for the evaporators, the exposed parts were of nickel. When the coagulation method was used, $Al_2(SO_4)_3$ was added in a glass-lined kettle.

Batch Process at Bitterfeld.—The reactor was charged with previously mixed water and emulsifier, vinyl chloride, and the catalyst, hydrogen peroxide. The temperature was controlled at 45°C. by means of a water jacket. Polymerization was complete in 24 hr. Remaining vinyl chloride monomer was flashed to the atmosphere. The emulsion was pumped directly to the iron spray dryers. They were heated with air at 160°C. The air was heated by fin-type steam exchangers. The cold emulsion was sprayed tangentially through 30 sprays at the top of the dryer. The dry, finely divided polyvinyl chloride was collected by a cyclone. The remaining 10 per cent was removed by means of vertical cotton bags. The dry polymer was then conveyed with screw conveyors to large iron storage tanks.

Continuous Process at Schkopau.—Two types of polymer were made. One for electrical applications was polymerized with hydrogen peroxide catalyst. The second was polymerized with $Na_2S_2O_8$ catalyst and used for all other purposes. Two types of drying were used at Schkopau; (1) spray drying as described for Bitterfeld and (2) coagulating, filtering, washing, compressing, and finally drying with hot air.

The glass-lined reactor was charged with the mersolate and water (which were previously mixed), vinyl chloride, and the catalyst. Emulsification took place in the first or upper few feet of the reactor. The temperature was controlled at 45°C. from top to bottom of reactor by means of a water jacket. Reaction time was 3.5 hr. with sodium persulphate and 5 hr. with hydrogen peroxide. From the bottom of the reactor the emulsion was pumped to a nickel helical spiral vacuum evaporator, where the excess monomer was flashed off, condensed, and recycled to the polymerizers.

The emulsion free of monomer was either spray dried or coagulated and dried by conventional methods. When the latter method was used, $Al_2(SO_4)_3$ was added in a glass-lined kettle and the suspension settled, decanted, and filtered on a continuous vacuum filter. The powder was washed on a belt as it passed to a second filter. Soda was added at this stage as a stabilizer. The damp powder was compacted on an aeriform continuous press. The resulting pellets were dried at 80°C. on a link screen belt, ground to a fine powder, and packaged.

Packaging

Finely powdered polyvinyl chloride was packaged in paper bags.

POLYVINYLIDENE CHLORIDE

Polyvinylidene chloride and its copolymers, known as Saran, are often used for handling troublesome chemicals, but in the making of this resin special materials of construction are required. Nickel is used extensively in processing for both vessels and piping. Inconel and nickel are used for handling the wet polymer, as it is necessary to preserve the clear color and protect it from the yellowing effect induced by certain metallic impurities. Later when the dry Saran products are being extruded, dies of Z nickel are used for extrusion. Blenders are made of nickel-clad steel. (Anon., Dow Chemical Co. and the Salts of the Earth, *Inco Process Ind. Quart.*, Vol. 11, No. 2, p. 6, 1948.)

Glass-lined steel reactors and many tanks are in use for the production of polyvinylidene chloride.

POTASSIUM CHLORIDE

Potassium chloride, also known as muriate of potash, is obtained from natural deposits centering around Carlsbad, N.M., and Searles Lake, Calif. As might be expected it behaves toward the various materials of construction much like sodium chloride or common salt.

Production

Materials of Construction.—Piping is generally cast iron, ordinary steel, terra cotta, wood, Monel, rubber, or rubber-lined steel. Heat exchangers are made of steel with charcoal iron or steel tubes, or they may be made of Monel. The evaporators are cast iron or steel with Monel tube sheets and tubes. Filters are generally Monel or cast iron with Monel cloth. Centrifuges have bronze, steel, Monel, nickel, or Inconel baskets. Dryers are steel. Agitators are steel with cast-iron blades.

For bins and hoppers, steel is ordinarily used. Classifiers are steel. Conveyors, crushers and grinders, crystallizers, and such tanks as those used for settling, storage, and washing are all made of steel. Condenser tubes are Monel; screens are 18-8 stainless steel. Valves and fittings are cast iron with stainless-steel trim.

Some plants use 20 per cent nickel Ni-Resist (copper-free) pumps; others prefer cast iron. In yet other plants Worthite or Durimet pumps and valves are used for handling evaporator discharge, crystallizer feed, and the filter-press transfer.

Crystallization Process.—The sylvinite is mined by ordinary underground methods, crushed, and charged into large leaching tanks where it is leached with mother liquors from a previous step in the cycle. (Badger, W. L., and E. M. Baker, "Inorganic Chemical Technology," 2d ed., p. 213, McGraw-Hill Book Company, Inc., New York, 1941.) This operation is carried out as near the boiling point as possible, in this case at 110°C. The solution is filtered and charged hot into vacuum crystallizers, where it is cooled by flash evaporation in a vacuum. Since this removes water, it would tend to precipitate both potassium and sodium chlorides, but enough water is fed to the crystallizer to correspond to the amount flashed off, so that no sodium chloride separates. The cooled solution is filtered on a rotary vacuum filter, which removes the potassium chloride crystals. These crystals are washed and dried on the filter. The mother liquor is reheated and used to leach the next batch of salt. This mother liquor, after coming into equilibrium with the mixed salt at 110°, should dissolve only potassium chloride, leaving the sodium chloride in the ore undissolved to be discarded after leaching.

Flotation Process.—The other large operator at Carlsbad uses a flotation process. (*Ibid.*) Sylvinite is not a double salt or a true mixed crystal in the sense of an intermolecular dispersion of two compounds. If the ore is crushed to about 40 mesh, the sodium and potassium chlorides are all in separate fragments. A flotation agent has been found that permits carrying off the sodium chloride in the froth while the potassium chloride is discharged from the bottom of the flotation cell.

Handling

See Sodium Chloride. The handling of potassium and sodium chlorides are similar as far as materials of construction are concerned.

POTASSIUM CYANIDE

For a 35 per cent solution at temperatures not exceeding 180°F. one plant uses Type 317 stainless steel for all tanks and pipe lines. Pumps are made of Worthite or Durimet. The shaft and impeller of an agitator in one of the plant's tanks are made of mild steel metallized with Type 317 stainless steel. A centrifuge separating KCN crystals from its mother liquor is made of plain low-carbon steel. The stainless-steel equipment is probably not necessary where the iron content of the potassium cyanide is not important.

Hard or soft rubber can handle solutions up to saturation at 150°F.

Potassium cyanide solutions under normal conditions are practically without action on all woods.

POTASSIUM HYDROXIDE .

In general, both potassium hydroxide and sodium hydroxide act similarly on materials of construction. However, one manufacturer of both caustics has found from experience with their action on iron that in some instances potassium hydroxide is more corrosive and in other cases caustic soda is harder on the iron and steel equipment.

Production

Materials of Construction.—Nickel and cast iron are often used for the equipment. Nickel equipment includes agitators, condensers, condenser tubes, heat exchangers, and screens. Either nickel or nickel-clad steel is used for crystallizers and evaporators.

In the case of centrifugals, steel is used for cold liquors below 20 per cent caustic; otherwise nickel is employed. Kettles are cast iron. Piping handling solutions of 20 per cent caustic solutions is nickel. Copper-free Ni-Resist is used for pumps. Aging tanks are ordinary steel. Settling tanks are steel for weak caustic solutions but nickel-clad steel for strong caustic.

Steel storage tanks are used for cold liquor. Thickeners handling cold liquor are steel; otherwise they are nickel or nickel-clad steel. Valves and fittings are nickel or Ni-Resist.

Silver is used in the production of the purest grades of both fused caustic potash and soda.

In the Trona process used to recover caustic from Searles Lake brines by American Potash & Chemical Corp. most of the material requirements are successfully met by cast iron and steel, with occasional use of nonmetallic materials, stainless steel, and copper alloys. (Anon., Potash, *Chem. & Met. Eng.*, Vol. 41, No. 10, p. 528, 1934.)

Underground piping is of cast iron, wood, or stoneware. Steel or cast iron serves for overhead piping, and cast iron or terra cotta for sewer lines. Both charcoal iron and seamless-steel tubing are used for heat-exchanger tubes, together with some admiralty metal. For the evaporators, steel or cast-iron bodies and heaters have proved satisfactory.

Cast-iron centrifugal pumps with steel shafts are generally employed, although a few pumps with stainless- and other alloy-steel impellers have been tried. Durimet 20 pumps are used on this service. Both bronze and steel have been used for centrifugal baskets, and cast iron for filters, with Monel-metal cloths. Unlined steel-plate construction is used successfully for the rotary dryers.

Similarly, cast iron and steel are the materials used at nearly all points in the production of potash from sylvinite. Steel is used for the storage bins, piping, and coolers, and cast iron for the digesters and evaporative crystallizers.

Handling

Solutions of potassium hydroxide in all but the lowest concentrations (below 0.01 per cent) rapidly attack aluminum and its alloys. For the dilute solutions, this attack can be inhibited by the addition of suitable chemical inhibitors, but in the more concentrated solutions none of the usual inhibitors are very effective. It also corrodes tin, lead, and zinc and their alloys. Caustic potash is noncorrosive to iron and does not affect rubber at room temperature.

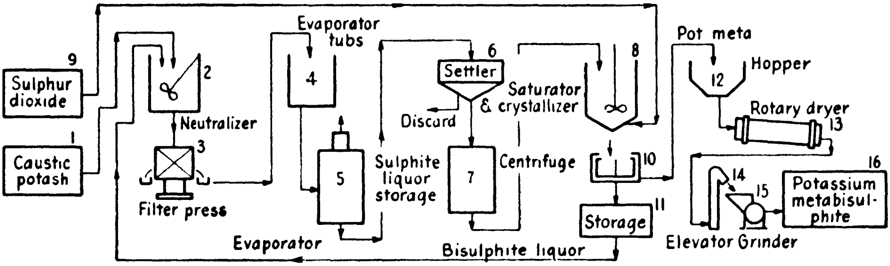
For additional information see Sodium Hydroxide.

Packaging

Caustic potash is shipped in steel drums, motor tank cars, and railroad tank cars.

POTASSIUM METABISULPHITE

Potassium metabisulphite, familiarly known as "pot meta," is actually the potash cousin of anhydrous bisulphite of soda. The two products have much in common, especially their corrosive action in most processing equipment. (Wheaton, G. S., and R. S. Sunderlin, Materials of Construction in a Metabisulphite Plant, *Chem. & Met. Eng.*, Vol. 52, No. 11, p. 231, 1945.)



Potassium metabisulphite.

1. Carbon steel
2. Chemical lead-lined, stainless-steel agitator
3. Wood
4. Lead-lined
5. Stainless steel
6. Lead-lined
7. Carbon steel
8. 18-8 Mo stainless steel
9. Steel
10. Stainless-steel basket
11. Urea-formaldehyde resin-coated steel
12. Wood
13. Stainless steel
14. Steel
15. Steel
16. Steel with fiber drums

Production

Materials of Construction.—Actually, the complicating factors in this little game of corrosion hide-and-seek are legion. They include acidity or alkalinity; concentration and physical state of each raw material, intermediate product, final product, and by-product; temperature and sometimes pressure; time of contact; combination of physical states; catalytic action; type and amount of agitation; and, of course, nature and combination of construction materials used. (*Ibid.*)

The preferred materials include lead and lead-lined steel and an 18-8 moly stainless. These materials proved satisfactory for most equipment, although ordinary steel, a urea-formaldehyde resin coating, and a few other materials were also used.

Process.—The process consisted of neutralizing caustic potash with bisulphite solution and saturating the resulting normal sulphite with SO_2 to yield pot meta. The principal raw materials are 50 per cent caustic potash and a bisulphite solution from the neutralization of normal potassium sulphite with liquid SO_2. The caustic is stored in ordinary steel tanks from which it is pumped into the neutralizing tank. Here the small amounts of iron compounds are converted into ferric hydroxide.

Actually, the neutralizing liquor contains some bisulphite, excess SO_2, and a host of by-product chemicals in small amounts. Acidity of the liquor is about pH 4, and the $KHSO_3$ content corresponds to saturation. The neutralizing tanks are lined with chemical lead; wood proved unsatisfactory because of the acidity and dehydrating effect. The agitators are either stainless steel or lead-coated. Care must be taken to provide good agitation and always to have an excess of bisulphite in the vessel; otherwise the caustic potash will dissolve some lead, an impurity particularly objectionable for the food- or photographic-grade product.

Neutralized liquor, now having a pH of about 6.1 and consisting essentially of 35 per cent normal potassium sulphite together with a slight excess of bisulphite, is pumped through a wood plate-and-frame press to remove precipitated iron and other solid impurities. The filtrate goes to the evaporator feed tanks, which must be lead-lined, since the hot liquor is not completely neutralized and has a dehydrating effect on wood. Iron pickup must be carefully avoided.

The vacuum evaporator, in which the concentration of normal sulphite is raised to approximately 40 per cent on a weight basis, is stainless steel. The heat exchanger is 18-8 moly stainless steel, use of which is largely necessitated by the increased corrosiveness of bisulphite and liberated SO_2 at the higher temperature. Maximum temperature in this step is about 160°F.

Settling tanks, in which precipitated salts such as K_2SO_4 and sludge settle out, are rectangular in shape and lined with lead. Temperature of the solution is now about 125°F. The storage tanks for the settled liquor, now containing only normal sulphite and essentially neutral (pH about 6), are made of ordinary steel.

Normal potassium sulphite liquor is pumped into the heated saturator into which SO_2 is fed with constant agitation until the chemical absorption of SO_2 is complete and the normal sulphite is converted into the meta compound. The pH during the reaction is from 6 to 4; the maximum temperature is 195°F.

Liquid SO_2 is stored in the customary iron or steel cylinder. The saturator-crystallizer is a jacketed 18-8 moly stainless-steel vessel. After several years of constant use, attack on this vessel and stainless-steel lines has been so slight that the shine of the steel has not been taken off. An 18-8 moly pump has shown no corrosion after 4 years, whereas an ordinary 18-8 sleeve was corroded out within a week. The slurry of potassium metabisulphite crystals is then cooled and dropped into a centrifuge having a stainless-steel basket.

Cooled liquor from the centrifuge contains dissolved $KHSO_3$ and is still very corrosive to ordinary steel. The bisulphite storage, therefore, consists of a steel tank lined with a plastic coating of the urea-formaldehyde type. This type vessel provides the necessary protection against corrosion and contamination and yet is cheaper than one of the special stainless steels. This bisulphite liquor is recycled to be neutralized with caustic potash to provide normal sulphite.

Wet meta crystals pass through a stainless-steel continuous rotary dryer at about 135°F. The crystals enter with 5 per cent moisture and leave with less than 0.1 per cent moisture. Pot meta is sensitive to temperature so that good control of the dryer is necessary. Once decomposition starts, it will continue spontaneously in the presence of air, since the free sulphur liberated burns to SO_2 and thereby produces sufficient heat to free additional sulphur. At ordinary temperatures, metabisulphite is quite stable.

From the dryer, the granular pot meta, which dissolves more readily than coarse crystals, goes to a steel elevator which feeds a rotary hammer-mill grinder. The product is stored in regular steel hoppers.

Packaging

Potassium metabisulphite is packaged in fiber drums for shipment.

POTASSIUM PERCHLORATE

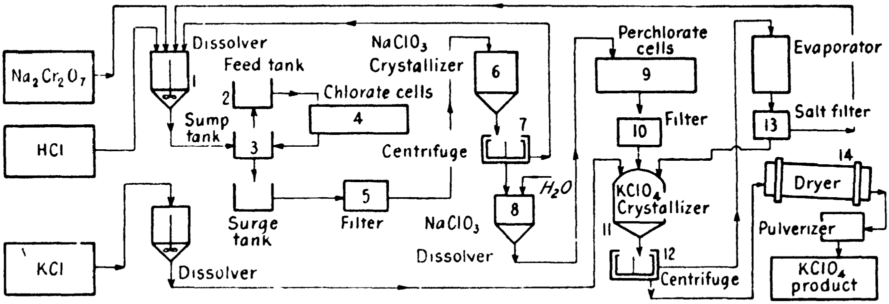
Chlorates are produced in extensive volume in the United States. Formerly, this country depended upon foreign sources for its requirements.

Production

Materials of Construction.—A brick-lined steel tank is used for dissolving the raw materials, and another of the same materials for the sump tank. Tygon-lined tanks are used for the feed tank to the sodium chlorate cell and for the filter. The sodium chlorate cell contains mild-steel cathodes and graphite anodes. The sodium chlorate crystallizer is nickel. The centrifuge is nickel and stainless steel. The sodium chlorate crystals are dissolved in a brick-lined steel vessel. The perchlorate cell may have steel cathodes and platinum anodes. The liquor from the cell may be filtered in a steel and aluminum filter. Piping is glass, porcelain, stoneware, or high-silicon iron. Nickel may be used for the crystallizer and salt filter. The centrifuge may be nickel and stainless steel.

Process.—The process used by Western Electrochemical Co. has been described. (Schumacher, J. C., Continuous Electrolytic Process for Perchlorate, *Chem. & Met. Eng.*, Vol. 51, No. 12, pp. 108–109, 1944.) It is carried out in three steps. In the first step, production of sodium chlorate is accomplished by continuously feeding a solution high in chloride and low in chlorate into the electrolytic system while an equal portion of the system liquor high in chlorate and low in chloride is simultaneously pumped out. In actual practice the circulating mother liquor from the sodium chlorate centrifuge is pumped to a dissolving tank for addition of sodium chloride. This feed liquor goes to a sump tank and then to a feed tank for the cells.

Electrolysis is carried out continuously with the conversion of the chloride to chlorate. Liquor from the cells is conducted back to the sump tank for recirculation. A portion of the liquor is withdrawn to a surge tank. Here the graphite is allowed to settle out. The clear liquor is filtered and pumped to the crystallizer. The mass goes to a centrifuge. Sodium chlorate crystals are washed and stored for the next step.



Potassium perchlorate.

1. Brick-lined steel
2. Tygon-lined steel
3. Brick-lined steel
4. Mild-steel cathodes, graphite anodes
5. Tygon-lined steel
6. Nickel
7. Nickel and stainless steel
8. Brick-lined steel
9. Steel cathodes, platinum anodes
10. Steel and aluminum
11. Nickel
12. Nickel and stainless steel
13. Nickel
14. Stainless steel

In the second step, production of sodium perchlorate is begun by dissolving sodium chlorate in water and allowing it to flow to the perchlorate electrolytic system. Pumping, cooling, and pump-out designs are identical with those of the chlorate system except that a smaller volume of liquor is handled and the cell characteristics are different. Concentrated sodium perchlorate from the cells must first be treated in a tank for removal of reagents used in processing. It is then ready for the final step.

Production of potassium perchlorate is performed in a crystallizing tank. Filtered potassium chloride solution is added to the sodium perchlorate liquor, and potassium perchlorate crystals are precipitated from the solution. These are removed from the crystallizer, centrifuged, and washed. The washed perchlorate is conveyed to a continuous dryer and is then pulverized and packaged.

Packaging

Potassium perchlorate is shipped in moistureproof multiwall paper bags or in steel drums.

POTATO FLOUR, WHITE

Production

Materials of Construction.—There are no corrosion problems here. Plain steel is satisfactory.

Process.—In drying potatoes by the flaking process for the manufacture of potato flour the procedure is as follows. (Noel, W. A., Manufacture of White Potato Flour, *Chem. Age*, Vol. 30, No. 9, pp. 381–384.) U.S. No. 2 potatoes are washed, mechanically peeled, trimmed and sorted, steamed until soft usually in an autoclave at 15 lb. pressure for 15 to 20 min., washed, spread in a thin layer on the surface of a revolving hot steel drum, dried, and removed from the drum continuously, then ground to a powder and bolted. The drying drum consists of a large revolving steel cylinder with a smooth surface. It is heated by steam confined within the drum.

Small steel rollers spread the washed potatoes in a thin layer on the surface of the drum. Stripper blades set against the drum remove dried flakes.

PROPIONIC ACID—ACETIC ACID

High-silicon iron valves are in use for handling a mixture of 30 per cent acetic acid and 70 per cent propionic acid at a temperature of 150 to 160°F.

PYRIBENZAMINE

Pyribenzamine is an antihistaminic drug which in some way prevents or modifies the action of histamine, bringing about symptomatic relief. It is a coal-tar derivative.

This drug is produced in glass-lined and stainless-steel equipment. (Bassoe, H., Bedeviled Hay Fever Victims Find Relief, *Glass Lining*, Pfaudler Co., Vol. 17, No. 2, pp. 2–5, 1946.) Crude distilling of pyribenzamine base in special insulated units is done prior to purification and crystallization. The final purification is completed in a battery of glass-lined open jacketed kettles in the Summit, N.J., plant of Ciba Pharmaceutical Products, Inc.

RHUBARB

To prepare dehydrated rhubarb it is trimmed, washed, cut in pieces, spread on Monel or other resistant metal screen trays, steamed 3 to 4 min., and dehydrated at not above 160°F. to low-moisture content. Or the pieces may be blanched in steam or in boiling water about 2 min. and spread on wooden-slat trays.

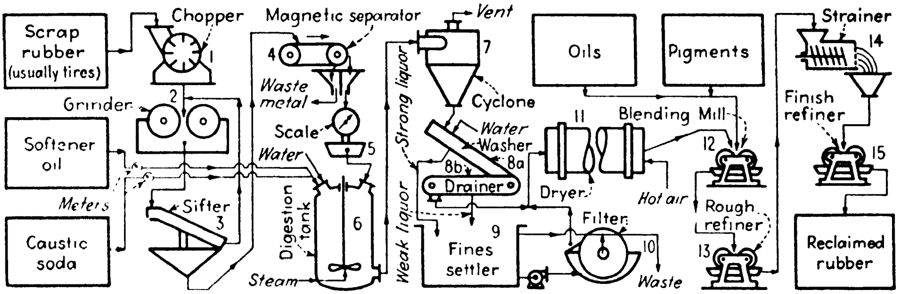
Galvanized screen must not be used, as the acid dissolves the zinc coating.

RUBBER, RECLAIMED

Rubber is recovered from old tires, inner tubes, and other used articles. It is used in manufacturing certain rubber items such as shoe soles. Both natural and synthetic rubber are reclaimed.

Production

Materials of Construction.—As the only chemicals used in the recovery of rubber are caustic soda and oils, no special materials of construction are demanded.



Rubber reclaiming.

1. Cast-iron frame and housing, forged-steel rotor and high-carbon steel knives
2. Chilled cast-iron rolls
3. Sheet steel
4. Rubber belting
5. Steel hopper
6. Steel plate
7. Sheet steel

8*a*. Stainless-steel screen cloth and steel frame

8*b*. Cast iron

9. Wood-stave tanks
10. Cast-iron frame filters with wood-stave drums
11. Steel plate
12. Chilled cast-iron rolls
13. Chilled cast-iron rolls
14. Cast-iron body with forged-steel screw
15. Chilled cast-iron rolls

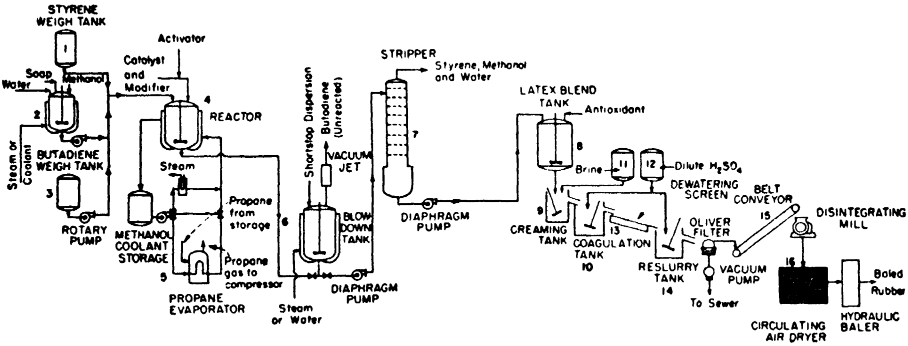
Process.—The scrap-rubber articles such as tires are first chopped and then ground between chilled cast-iron rolls. After the scrap has passed over a rotary sifter to separate the coarse particles, the fine material is conveyed over a magnetic separator. After the metal particles are removed, it is weighed and charged into the steel digester. The digester may be either horizontal or vertical. Softener oil and caustic soda are metered and pumped into the digester. The mass is agitated and heated by steam. When digestion is completed and the cotton dissolved, the mass is washed over a stainless-steel screen cloth on a steel frame. The fines settle in a wood stave tank and pass to either a rotary vacuum filter or vibrating screens. The solids are dried in either rotary or Sargent dryers. The dried rubber is then refined.

RUBBER, SYNTHETIC (GR-S)

Most of the synthetic rubber is produced from butadiene and styrene and is known as GR-S.

Production

Materials of Construction.—Storage tanks, kettles and soap crutchers, valves, pumps, and piping are notable applications of stainless steel. Mixing vats, agitator blades, heat and pressure chambers, and heat-exchanger tubes illustrate other uses for stainless steel in synthetic-rubber production. Vibrating screens of stainless steel solved the difficult problem of separating rubber crumbs from the acid-salt solution.



Synthetic rubber.

1. Carbon steel
2. Glass-lined steel
3. Carbon steel
4. Glass-lined steel, stainless
5. Carbon steel
6. Glass-lined steel
7. Pyrex glass, glass-lined steel
8. Glass-lined steel, concrete
9. Wood
10. Wood
11. Glass-lined steel
12. Glass-lined steel
13. Stainless steel
14. Wood
15. Rubber
16. Stainless-steel trays

Glass-lined steel is used to a large extent in the production of GR-S rubber. Glass-lined reactors and agitators prevent the rubber from adhering to the equipment and causing serious operating difficulties. The hardened rubber must be chipped off the surfaces of steel. A glass-lined latex flash tank is used as well as storage tank and blowdown tanks. The catalyst is dissolved in a glass-lined tank. This same construction is also used for catalyst weigh tanks and feed tanks. Protective agent tanks, too, are glass-lined.

Ordinary steel is used for soap storage, activator storage, and other purposes. Wood is used for fabrication of the creaming and coagulating tubs for the latex and for reslurry tanks, soap-preparation tanks, and activator-solution make-up tanks.

Low-temperature Process.—One of the first steps in the process is the removal of the polymerization inhibitors in the butadiene and styrene raw

Department of Agriculture. This work has resulted in several commercial plants. Two processes have been developed: (1) the hot-water extraction process and (2) the dilute-alcohol extraction process.

Production

Materials of Construction (Hot-water Extraction).—In this process it is suggested (Eskew, R. K., *et al.*, Production of Rutin from Buckwheat Leaf Meal, AIC—114, Eastern Regional Research Laboratory, 1946) that the following materials and equipment be used: wooden tank for water heating system for extraction, wood leaching tank, wooden storage tank for extracts, stainless-steel evaporator with jet condenser, wooden holding tank, wooden coagulating tank, cypress filter press for curd, stainless-steel evaporator (condenser and receiver may be copper), wooden dissolving and crystallizing tanks, stainless-steel crystal filter press, stainless-steel filter press for hot filtrations, stainless-steel tank for dissolving rutin crystals in alcohol, wood-dissolving tank for crystals in the butts after removal of alcohol, and stainless-steel tank for final crystallization.

Materials of Construction (Alcohol Extraction).—Materials and equipment suggested by the authors are as follows: wooden extraction tanks, wooden holding tank for extracts, stainless-steel evaporator, wooden dissolving tanks, stainless-steel filter press for removing tars, wooden crystallizing tanks, stainless-steel crystal filter press, stainless-steel filter press for hot filtrations, stainless-steel tank for dissolving rutin crystals in alcohol, wooden dissolving tank for crystals in the butts after removal of strong alcohol, stainless-steel tank for third crystallization, stainless-steel benzol extraction unit, steel storage tank for alcohol recovered from evaporation of leaches, steel tank for preparing 70 per cent alcohol, aluminum storage tank for weak alcohol recovered from marc, small stainless-steel evaporator, and steel benzol storage tanks.

Hot-water Extraction Process.—Buckwheat leaf meal is given three extractions in boiling water to remove the rutin. After extractions are filtered, they are concentrated by vacuum evaporation. Proteins and colloidal materials are coagulated by adding an equal volume of 95 per cent ethyl alcohol to the concentrates. The curd so formed is removed by filtration; the filtrate is evaporated with addition of water until all alcohol is driven off. This water solution is permitted to crystallize, and the crude rutin is filtered off. A recrystallization is then given. If traces of alcohol insolubles are objectionable in the finished rutin, they can be removed at this point by dissolving the rutin in a small amount of hot alcohol and filtering; thereafter in a vacuum evaporation step the alcohol is replaced by water. A third and final crystallization is then given to ensure the desired purity, after which the crystals are filtered off and dried.

Dilute-alcohol Extraction Process.—In the extraction with dilute alcohol (70 per cent), meal is given three extractions at room temperature. Extracts are concentrated by vacuum evaporation. Since fats and tars are extracted from the meal by dilute alcohol, they must be removed. The hulls of these can be eliminated by hot filtration. Filtrates are then purified by the same process used in hot-water extraction with certain exceptions.

SALAD DRESSING

The handling and processing of highly acid and corrosive products, such as brines and other mixtures containing vinegar and salt, have always presented difficulties. There are few commercial metals that will withstand the vinegar-salt combination in salad dressings.

Production

Materials of Construction.—The oils are handled in black-iron equipment. Vinegar is stored in wooden tanks and handled by stainless-steel pumps, pipe, and valves. The processing of these and other raw materials that go to make up the salad dressing is done by stainless-steel equipment.

Inconel, 18-8 stainless steel, and the 17 per cent chromium steel are the most suitable materials for whips and beater bowls in contact with mayonnaise at atmospheric temperature, because all are immune to significant attack and free from tarnish. Nickel and Monel are less suitable chiefly because of their tending to tarnish, which may or may not be considered a serious objection. (Mason, J. F., Jr., Resistance of Alloys to Corrosion during Processing of Some Foods, *Corrosion*, July, 1948.) The manufacture of cooked salad dressing requires the use of materials for the cooking kettles that can withstand the effects of prolonged contact with boiling solutions of vinegar and salt. Such mixtures are very corrosive. Monel, nickel, and Inconel exhibit rather high rates of corrosion, and the 18-8 stainless steels, though they possess low rates of attack as measured by weight loss, are subject to rather severe local attack.

Experience has demonstrated, however, that 18-8 molybdenum stainless steel, Type 316, is the best choice for handling such mixtures. (*Ibid.*) Even so, this stainless steel shows some tendency toward pitting which can be kept to a minimum by having the surface of the steel as highly polished as possible and by cleaning the surfaces to remove acid salty solids after each use.

Process.—A highly integrated continuous-processing system for the manufacture of dressing products is being operated by Durkee Famous Foods in its plant at Norwalk, Conn. (Ziemba, J. V., High Efficiency Attained on Multi-Product Line, *Food Ind.*, Vol. 21, No. 3, pp. 292–294, 423–424, 1949.) Blended oils, chiefly corn and cottonseed, are delivered to the plant in tank cars. Black-iron pipes and fittings and a centrifugal pump are used to unload the tank cars. The oil is then pumped directly into black-iron storage tanks.

Distilled, aged-in-wood vinegar arrives at the plant in wooden tank cars. It is pumped by a stainless-steel centrifugal pump through stainless-steel pipes into cypress tanks. Other raw materials are received in a variety of containers and stored.

Salad dressing is a mixture of starch paste and mayonnaise—an emulsion of starch paste and vegetable oil, using egg as the emulsifying agent. The paste is prepared by cooking the starch slurry and then cooling the paste before it is added to oil, spices, and eggs in the premixer.

The starch-slurry mix is prepared in a stainless-steel slurry tank, which is equipped with a portable propeller mixer and set upon a tank scale. Water and vinegar are first weighed into the tank, then starch, stabilizer, salt, and sugar. This starch-slurry mix is then pumped into a stainless-steel holding tank. Durimet 20 is giving excellent service as mixing equipment for mayonnaise and salad dressing.

A steady flow of slurry from the holding tank through the Votator processing equipment is provided by a piston pump. Here, the slurry is cooked and cooled. Each unit consists essentially of concentric tubes which form two annular spaces around a central agitating shaft. The heat-transfer medium flows through the outer space, the product through the inner one around the shaft, and the heat passes through the tube wall from one to the other. To conserve heat, the outer tube is jacketed with insulation, which, in turn, is covered with stainless steel.

From the cooking and cooling units, the paste flows into stainless-steel gelling tanks. These tanks permit further gelatinization and hold the paste ready for the premixers.

Salad dressing, sandwich spread, and mayonnaise are prepared in the premixers, which are equipped with impellers. In the manufacture of salad dressing, starch paste is pumped through a preset recording meter to stainless-steel premixers. Here, too, metered quantities of cooled salad oil are delivered from oil-storage tanks and mixed with eggs, starch paste, and combination spice oils. Mayonnaise and sandwich spread are also prepared at this point. Starch paste is omitted from the mayonnaise formula, while vegetable relish is added to a mayonnaise base in the production of sandwich spread.

From premixers, dressing products are continuously discharged through a mayonnaise machine, which completes the emulsification. Mayonnaise, salad dressing, and sandwich spread then flow continuously to the packaging line.

Handling

Notwithstanding the corrosive character of these combinations, they are successfully handled with 18-8 stainless steel. But on account of the unusually corrosive nature, precautions must be observed to wash and rinse thoroughly all equipment after use; otherwise pitting may eventually occur. (Mitchell, W. M., Steel Alloys, *Food Ind.*, Vol. 7, No. 12, pp. 577–579, 1935.)

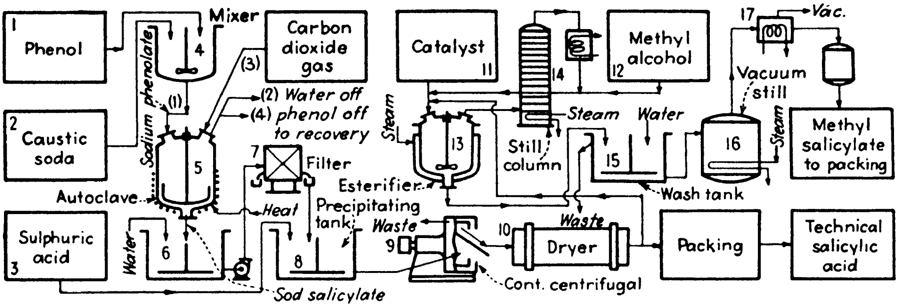
Salad dressings are handled to advantage in glass-lined equipment where the highly corrosive effects of vinegar are nullified. (Barnes, P. S., Glass-lined Equipment, *Food Ind.*, Vol. 7, No. 12, pp. 591–592, 1935.)

SALICYLIC ACID

This chemical is an old and well-known organic compound. Although used in direct form in certain types of pharmaceutical preparations and as a preservative for glues and leather goods, its major use is as an intermediate in the synthesis of dyes and other organic compounds.

Production

Materials of Construction.—Wood is in use for such equipment as sodium salicylate treatment tanks and for salicylic acid precipitation tanks. Plain iron is used for the tank in which the sodium phenolate solution is prepared. Chlorimet 3 pumps and miscellaneous equipment were used by one plant for this solution, since extreme purity was desired.



Reactions:

$$2C_6H_5OH + 2NaOH \rightarrow 2C_6H_5ONa + 2H_2O$$
$$2C_6H_5ONa + CO_2 \rightarrow ONaC_6H_4COONa + C_6H_5OH$$
$$ONaC_6H_4COONa + H_2SO_4 \rightarrow OHC_6H_4COOH + Na_2SO_4$$
$$OHC_6H_4COOH + CH_3OH \rightarrow OHC_6H_4COOCH_3 + H_2O$$

Salicylic acid and methyl salicylate.

1. Steel
2. Steel
3. Lead-lined wood
4. Steel
5. Steel
6. Wood
7. Wood
8. Wood
9. Rubber-lined steel
10. Stainless steel
11. Steel
12. Steel
13. Copper
14. Copper
15. Copper
16. Copper
17. Stainless steel

Process.—Phenol and caustic soda solution are received in tank cars and transferred to separate storage tanks. These materials are withdrawn in predetermined quantities to mixers, and a highly concentrated sodium phenolate solution prepared. The phenolate is desiccated, powdered finely, and carbonated in autoclaves with carbon dioxide. Conversion to sodium salicylate is the next step, and after the charge is dissolved in water, it is blown or pumped into large wooden treatment tanks. After purification in these tanks, the solutions are filtered and discharged by gravity into wooden precipitation tanks. The slurry of precipitated salicylic acid then flows by gravity to continuous centrifugals, where the technical salicylic acid is separated from the mother liquor, washed, and discharged. The moist acid is dried in rotary dryers whence it is delivered to other departments.

Handling

Aluminum is used for columns, condensers, piping, and pumps for salicylic acid. (Brown, H., *et al.*, "Aluminum and Its Applications," p. 289, Pitman Publishing Corp., New York, 1948.)

Copper is in use for evaporators and piping. Bronze can also be used to handle salicylic acid.

Durimet 20 is resistant to the acid at all temperatures and concentrations and is said to be superior to 18-8 stainless steel, which is not generally satisfactory.

Silver is used to line vessels for the acid. (French, H. J., Metals to Resist Corrosion or High Temperatures, *Trans. A.E.S.*, Vol. 50, pp. 47–89, 1926.)

Packaging

Salicylic acid is shipped in wooden or fiber drums.

SAUERKRAUT

Several metallic and nonmetallic materials are useful in handling and processing sauerkraut.

Production

Materials of Construction.—Wooden trays, tanks, and other equipment have long been used. Redwood tanks have long had an extensive usage in the brine processing and storage of sauerkraut. (California Redwood Association, *Tech. Bull.* 16–5.)

While sauerkraut has little if any effect on concrete, a surface coating (magnesium fluosilicate or zinc fluosilicate, or sodium silicate) should be used to protect the taste. (Boase, A. J., Concrete for Structures and Equipment, *Food Ind.*, Vol. 7, No. 12, p. 589, 1935.)

Type 18-8 stainless steel is used for sauerkraut juice. Monel is also used in the processing.

Process.—To prepare dehydrated sauerkraut cabbage is shredded in a kraut slicer and is converted into sauerkraut by the usual procedure by fermenting with 2½ per cent of salt. It is then drained, trayed on Monel screens, steamed, and dehydrated at not above 150°F. to less than 5 per cent moisture. Or it may be steamed and spread on wooden trays for drying.

SIRUP

Here are some interesting comments on the handling of nonacid and acid sirups. These sirups are encountered in beverages, canned foods, fruit juices, jams, jellies, and preserves.

Handling

Metals commonly used for water lines are not satisfactory for sirup handling. (Scharf, J. M., How to Avoid Contamination in Sirup Handling, *Food Ind.*, Vol. 8, No. 1, pp. 24, 43, 1937.)

The reason for this is that the acidifying agents and the sterilizers generally used seriously corrode these metals. This results in metallic contamination of the sirups and, consequently, of the final beverage.

Stainless steel, glass-lined steel, nickel, and high-nickel alloys are the most universally satisfactory materials. Block tin and high-quality bronze are suitable in certain instances. Less applicable and suitable only under less severe conditions are aluminum, copper, and stoneware. In certain types of tubing for special purposes, glass and rubber are satisfactory. The table on page 312, from *A.B.C.B. Educational Bulletin* 9, shows the types of materials that have been found satisfactory for various types of sirup equipment.

To be absolutely safe, equipment should be made of materials that will withstand the most severe conditions encountered. Suppose equipment for handling a nonacidified simple sirup were made of some of the less resistant materials. It would be possible that, through accident or change in routine, an acid product might be put in such equipment. The result would be contamination of the product.

Pipe Lines.—Block tin tubing has been most used in the past for sirup piping because of its availability and the ease with which it can be formed and fitted. However, it is not universally the best material with respect to corrosion resistance. Also, it tends to become brittle with age, and unless it is continuously supported, it will sag, resulting in sections that do not drain properly. Tin coatings on stronger metals overcome these difficulties, but there is danger of contamination when the tin wears away and exposes the base metal.

Recently, thin tubings of high-strength and high-resistant metals like stainless steel have become available. These satisfactorily serve for all sirup piping. The tube walls are too thin for use with screw fittings, but welded, sweated, or compression fittings are used.

Heat-resistant glass tubing and glass-lined pipe are excellent for sirup lines, but being fragile, they need careful handling. Glass tubing has the advantage of the ease with which the contents can be examined.

Fittings.—The best fittings to use with the metal pipe lines are the sweated sleeve type. These give a sturdy, sanitary connection, without the dirt-catching crevice around the pipe end that occurs when the ordinary threaded fitting is used. A special threaded fitting is available which leaves a shoulder against which the pipe end butts, giving a smooth inner bore without any crevices. In practice, however, this latter type has proved to be too costly and is not entirely satisfactory.

Two other joints which depend on butting the ends of the tubing together, directly or with a light gasket, are the flange and the compression fitting. These give a practically unbroken bore when properly made. They are satisfactory and possess the additional advantage of being easily removable for inspection and cleaning.

Valves.—Of the valve designs that have the cleanest internal design, the plug cock and some of the newer diaphragm valves are interesting. Modern designs of sanitary plug cocks made of the corrosion-resistant metals have over-

SUITABILITY OF MATERIALS FOR CONSTRUCTION OF SIRUP EQUIPMENT

Use	Satisfactory	Fair	Unsatisfactory
Hot-process sirup *without* acid	Stainless steel * Glass enamel Nickel Nickel-copper alloy Block tin †	Aluminum Bronze ‡ Copper	Stoneware
Hot-process sirup *with* acid	Stainless steel Glass enamel	Nickel Nickel-copper alloy Bronze Block tin	Aluminum Copper Stoneware
Cold-process sirup *without* acid (storage of nonacid sirup)	Stainless steel Glass enamel Nickel Nickel-copper alloy Bronze Block tin Stoneware	Aluminum Copper	
Cold-process sirup *with* acid (storage of acidified sirup)	Stainless steel Glass enamel Nickel Nickel-copper alloy Stoneware	Bronze	Copper
Pipe lines Valves Fittings	Stainless steel Glass enamel Glass tubing Nickel Nickel-copper alloy	Bronze Block tin Aluminum Rubber hose (acid-resistant)	Copper
Carbonated water	Stainless steel Block tin Bronze Silver plate	Nickel Nickel-copper alloy	Copper Aluminum

* Stainless steel means both the KA2 and 18-8 types of steel, properly heat-treated and fabricated to give best corrosion-resisting properties.

† Block tin means either block tin or pure block tin over suitable base free from pinholes.

‡ Bronze means either high-quality silicon or aluminum bronze of high acid resistance.

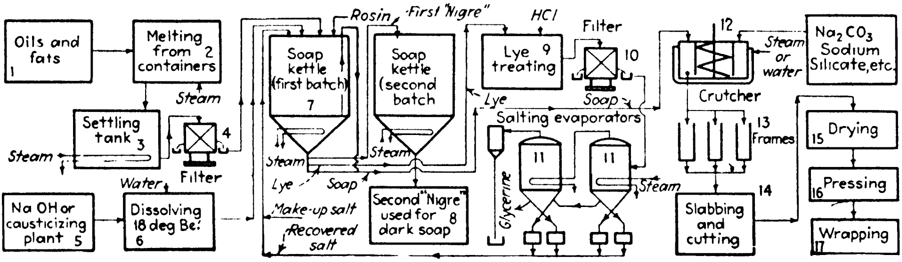
Complete report of the investigational work is given in the American Bottlers of Carbonated Beverages Educational *Bulletin*, Suitability of Materials for Sirup and Carbonating Equipment.

come the faults of the older standard designs. These valves are among the most sanitary, most easily cleaned and handled to be obtained.

The new diaphragm valves have a shutoff action depending upon a highly resistant rubber diaphragm being closed down on a slightly raised metal dam. The body of the valve is made of resistant metal. These valves are excellent for their sanitation, ease of adjustment and repair, and moderate first cost.

SOAP ,

One of the world's oldest process industries is soapmaking. For centuries soap has been made by the reaction of fat and lye. Until recently, most improvements in the manufacturing processes have been merely in more resistant materials of construction and increased size of equipment or better control devices, but no radical change had been made in the fundamental soap kettle.



Laundry soap.

1. Steel
2. Steel
3. Steel
4. Cast iron, cast aluminum
5. Steel, nickel
6. Steel, Monel
7. Steel; steel with top section nickel-clad or stainless-clad
8. Steel
9. Steel, cast iron, stainless-clad, nickel-clad, wood
10. Aluminum, steel, cast iron
11. All-nickel-clad evaporator and salt pot, cast iron with copper tubes
12. Cast iron, steel, stainless, stainless-clad
13. Cast-iron, steel, stainless-clad, stainless
14. Wood frame, piano-wire cutters
15. Steel
16. Steel
17. Steel

Pump: nickel cast steel, Worthite, cast iron

Piping: black iron, galvanized iron, steel, copper tubing; fatty acids: red brass, stainless steel

Agitators: cast iron, bronze, Monel, stainless steel

Production

Materials of Construction.—Equipment of the processes directly involved in the production of soap is mostly fabricated of carbon steel. This includes storage tanks for fats and oils, lye tanks, soap kettles, soap storage tanks, and crutchers. In general, ordinary steel stands up satisfactorily in this service, as soap builds up a protective film unless washed. Many manufacturers have not considered the additional cost of special corrosion-resistant material as warranted. On the other hand, there is an increasing trend toward the use of the stainless steels, nickel and its alloys, and other special materials, especially in the manufacture of high-quality white soap, such as white floating soaps, flake soaps, and toilet soaps. Elimination of any possibility of iron contamination resulting from the use of steel equipment or copper contamination resulting from copper or copper alloys avoids off-color soaps, development of change in odors, and development of rancidity. Even Monel is no longer used broadly in soap plants because of its copper content. It has been replaced to a large extent by both Types 316 and 317 stainless steels. The copper content of Monel makes it dangerous to use when handling soap because copper is the most active rancidity promoter experienced in the soap business.

For yellow and laundry soaps some manufacturers have found rolled steel satisfactory for soap kettles; others prefer flanged steel plates with the courses made of nickel-clad or stainless-clad steel. These same manufacturers have found that cast iron or steel plate has worn well for crutchers and agitators. Others are now using stainless or stainless-clad steel.

For filters, cast iron or cast aluminum is used. All plants use cast-iron salting evaporators, and some use copper tubes and tube sheets. For lye treating tanks wood, cast iron, or rolled steel is generally employed, but stainless-clad or nickel-clad is preferred occasionally. The pumps in laundry-soap plants are fabricated from cast iron with Ni-Resist or Monel trim. Some plants prefer acid-resistant bronze for handling slightly acid conditions and high-silicon iron for strong-acid washing. For soap, lye, and grease pipe lines, wrought iron (all-welded construction) is recommended. When piping fatty acids, stainless steel is used. Other laundry-soap companies use steel or galvanized iron for most pipe lines. For the storage of caustic soda prior to its use in the process, plain steel or nickel-clad steel tanks are used.

In the soap industry in general, important uses of corrosion-resistant materials are in the preliminary treatment and preparation of fats and oils for later processing. Fats and oils are sometimes stored in steel. Lead-lined tanks for acid washing of fats have long been used.

Twitchell process fat-splitting tanks have been constructed of steel or wood, lined with lead, but are usually cypress, unlined. This service is unusually severe, since the fat is boiled with water containing a low percentage of sulphuric acid. The fat and water levels change, and the tanks are alternately hot and cold. The hot fat shrinks the wood, and the hot water swells it. The cypress tanks are preferably mounted over lead trays to catch the leakage. Replacement of the tanks is rather frequent.

Redwood tanks are also used for producing fatty acid in the Twitchell process. Increased life can be secured if the heating coils are kept well away from direct contact with the wood. Consideration should be given to the use of lined redwood tanks for fatty-acid production. The linings can be lead or any other material inert to the solutions. The dry heat does not affect redwood, and the low thermal conductivity is helpful in maintaining temperature. The recently installed tanks for this purpose have been stainless-clad or nickel-clad steel. The use of these materials will no doubt result in an ultimate economy even though first cost is greater.

Fat-splitting autoclaves were formerly fabricated of copper, although steel was used in some cases when the fatty acids were to be distilled. Monel has been used, but more recent construction has been of Inconel, nickel-clad and stainless-clad steel. The use of these materials of construction permits the building of larger autoclaves and the use of higher pressures than was possible with copper autoclaves. They are preferred because scale forms on the bottoms of carbon-steel kettles.

There is a trend away from the use of copper and high-copper alloys in connection with fatty acids, especially in the final processing of the soap, where possible contamination of the soap with copper compounds is considered objectionable. However, copper is still used to some extent for bubble towers in stills.

Since corrosion in soap kettles seems to be most acute at and above the liquid line, existing steel or iron kettles have been lined around the upper sections with corrosion-resisting materials such as nickel or stainless steel in recent years by some manufacturers. In other cases manufacturers have used kettles fabricated completely of nickel-clad or stainless-clad steel.

Nickel is used widely in soap-boiling kettles for heating coils and spiders, pipe, fittings, kettle outlet valves, and suction lines. Existing iron pipes have been protected from corrosion by covering them with the light-gage Monel sheet. Monel-metal piping and steam-distributing spiders were first used in soap kettles in 1924. Examination of this piping 9 years later showed complete absence of corrosion in this service. Fume stacks on soap kettles in many plants are stainless-clad steel.

In some plants the salt is added to soap kettles in the form of a concentrated brine solution. Nickel-clad steel is used for these brine tanks, and pure nickel tubing in brine piping systems. In the handling of salt or brine, Monel is used extensively for salt hoppers and chutes and for brine pumps, brine lines, valves, and fittings. One of the earliest uses of Monel in soap plants was for pump rods in pumps handling fatty acids, lye, and brine.

In the case of heat exchangers for the handling of fatty acids at high temperatures, tubes, headers, and heater boxes may be Monel. Recent installations of fatty-acid distilling equipment have made extensive use of stainless steel, stainless-clad steel, and nickel for stills, condensers, separators, and pipe lines.

Filters are made of gray cast iron, ordinary steel, aluminum, or bronze depending upon the particular purpose. Filter cloth made of Monel is used on all types of filters in the soap plant. Plate-and-frame filter presses are mainly used; modern methods of gasketing Monel filter cloth have removed the difficulties of using metallic filter cloth in presses. In some cases Ni-Resist, of both the regular and copper-free varieties, is being used for filter press plates.

Perhaps the most serious corrosion problems affecting the life of equipment occur in the reclamation of the salts and glycerol. Even in these processes, the demand for a high-purity product may place more emphasis on freedom from contamination than upon life of equipment. Salting evaporators are sometimes constructed of cast-iron and copper tubes. In some plants nickel-clad steel is used for salt boxes with copper-free Ni-Resist doors. Modern toilet-soap factories use all-nickel-clad evaporators and salt pots to keep iron and copper out of the salt which is reused in the soap kettle. Glycerol bleach tanks are made of nickel-clad steel and galvanized steel.

Some miscellaneous equipment for the production of soap has been fabricated from metals which are highly resistant to corrosion. Stainless steel has been used for the tower construction for spraying soap powders. In some plants tile is used for this purpose. Crutchers, cutters, mixers, dies, pipe lines, wrapping tables, and much other equipment have been installed in Type 316 stainless steel, nickel, nickel-clad steel, or other corrosion-resistant materials.

Soap-cooling frames are frequently made of cast iron or steel plate or lined with stainless steel or nickel to prevent discoloration of the soap when it comes into contact with the sides of the frames. Saran screen cloth, framed, makes drying trays for soap. Stainless steel is used for the hoppers and working parts of plodders, which are employed for squeezing soap under high pressure into a solid bar of the required size and shape.

Amalgamators, which are used for incorporating perfume into the base, must be made of materials that are resistant to corrosion by perfumes and essential oils.

Drying is an important operation in the making of flake soap, and conveyors are generally employed for this purpose. The use of stainless-steel woven-wire belts for conveying flakes through the dryer prevents discoloration.

Spraying nozzles of Type 316 stainless steel are used on machines employed in the production of soap flakes. In these machines soap is forced under pressure through hollow forged cones fitted as a spray through fine holes drilled in the base of each cone. Stainless steel has proved in service to have the strength and resistance to corrosion necessary in this application.

For doctor blades on drying or chipping rolls several plants use cold-rolled, ¾ hard Inconel strip running against stainless-steel and chromium-plated rolls. Soap solutions in some plants are being handled in Worthite equipment.

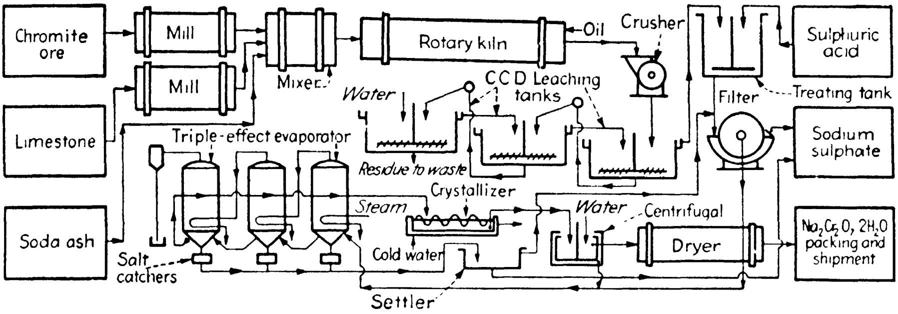
Continuous Soapmaking.—About the newest development in the soap industry is the several continuous processes for making soap. The process developed by the Procter & Gamble Co. (McBride, G. W., Continuous Process for Soap, *Chem. Eng.*, Vol. 54, No. 4, pp. 94–97, 1947) is continuous countercurrent hydrolysis under pressure and at high temperature with a catalyst, followed by continued distillation, neutralization, and finishing. In general, the equipment throughout the process is made of stainless steel where the fatty acids are at high pressure or temperature but of aluminum where at low pressure. Fats are split to yield fatty acid and glycerin in a hydrolyzer, a 65-ft. stainless-steel column. The fatty acids are continuously distilled under high vacuum in a stainless-steel vessel.

SODIUM BICHROMATE

There are no corrosion problems in the processing and handling of sodium bichromate. Ordinary materials are suitable, for sodium bichromate is an inhibitor of corrosion.

Production

Materials of Construction.—There are no difficulties in manufacturing sodium chromates or bichromates. Carbon steel is used throughout, even in contact with a solution which is 60 per cent bichromate and 1 to 5 per cent sulphuric acid.



Sodium bichromate. Plain carbon steel is satisfactory to use throughout the process, even after the chromate solution is oxidized with H_2SO_4 (60°Bé.). The product is itself a corrosion inhibitor.

Process.—The ore is ground to 200 mesh, mixed with ground limestone and soda ash, and roasted at 2200°F. in a strongly oxidizing atmosphere. The sintered mass is crushed and leached with hot water to separate the soluble sodium chromate. The solution is treated with enough sulphuric acid to convert the chromate to bichromate with the resulting formation of sodium sulphate. Most of the sodium sulphate crystallizes in the anhydrous state from the boiling hot solution during acidification, and the remainder drops out in the evaporators on concentrating the bichromate solution. From the evaporator the hot saturated bichromate solution is fed to the crystallizer, then to the centrifuge and dryer. (Shreve, R. N., "The Chemical Process Industries," 1st ed., pp. 437–438, McGraw-Hill Book Company, Inc., New York, 1945.)

Handling

Plain carbon steel and other common materials of construction are completely satisfactory.

Packaging

For shipping dry material paper bags are used, except in the case of material for export, when wooden barrels are used.

SODIUM BIFLUORIDES

Among the materials that are satisfactory for handling of sodium bifluorides are chemical lead, copper, Monel, and Saran. Natural rubber, carbon, and neoprene give excellent results. Mild steel is very subject to corrosion. (Callaham, J. R., Fluorine Industry, *Chem. & Met. Eng.*, Vol. 52, No. 3, p. 99, 1945.)

Packaging

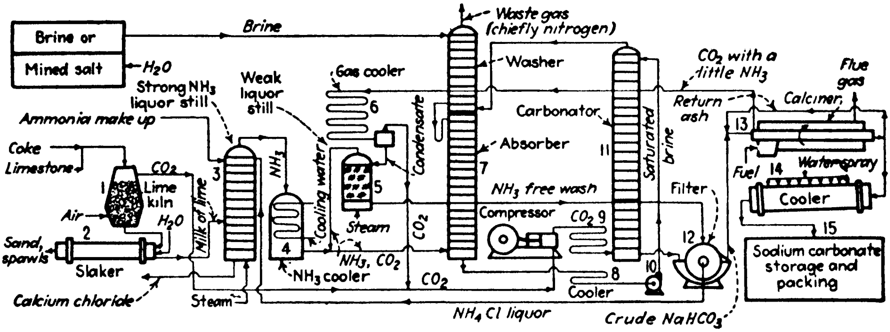
Sodium bifluoride can be packed in paper-lined barrels and fiber drums.

SODIUM CARBONATE

Soda ash is made by the Solvay (ammonium-soda) process. To a lesser extent the soda ash requirements come from natural brine of saline lakes in the Far West.

Production

Materials of Construction.—The material used for the construction of the equipment is limited. (Hou, Te-Pang, "Manufacture of Soda," 2d ed., Reinhold Publishing Corporation, New York, 1942.) Presence of ammonia in the gases and liquors unfortunately has eliminated the use of any copper, brass, or bronze materials, for copper and copper alloys are as a rule readily attacked by ammonia, showing a deep blue coloration. Steel and wrought iron lead very short



Soda ash (ammonia soda process).

1. Brick-lined steel
2. Steel with stainless-steel mechanism
3. Cast iron, stoneware spiral tiles, cast-iron tubes
4. Cast iron
5. Cast iron
6. Cast iron
7. Cast iron
8. Stainless steel, cast iron
9. Steel
10. Stainless steel, cast iron
11. Cast iron
12. Cast iron with nickel-wire cloth and wool felt
13. Steel
14. Steel
15. Concrete silos

lives in contact with ammonia gases or brine liquors containing ammonia and carbon dioxide, especially at elevated temperatures. The life of a steel tube in contact with hot ammoniated brine is from 6 months to a year, and that with cold ammoniated brine is from 1 to 2 years. Much trouble has been caused by the failure of cooling tubes made of standard boiler steel tubing.

Only cast iron will satisfactorily withstand the corrosion. Unmachined cast-iron surfaces having a hard crust stand the corrosion better than machined faces. Special grades of cast iron, *e.g.*, Meehanite, can be prepared which will withstand corrosion better than the ordinary grades. It is imperative that only cast-iron construction be used wherever possible; an all-iron construction is a familiar specification for ammonia-soda equipment.

Lead has excellent corrosion-resistant properties, but its softness limits its use to such matters as bell and spigot joint calking, gaskets for unmachined faces, cast-iron tubing expanding, and some low-pressure work.

High-silicon iron (especially Durichlor) is resistant to the action of ammoniated brines or ammonium chloride liquors. It is used in a limited number of places where the metal is not subject to mechanical or thermal strain.

Stainless steels resist corrosion eminently well, although toward hot ammoniated brine they are not so good as the high-silicon iron Durichlor. Type 304 stainless steel (0.05 to 0.06 per cent carbon) is especially recommended, although some other grades, such as Type 317, are more resistant and more costly. It is esesntial that these stainless steels be heat-treated after all heating operations. Only the stabilized stainless steels can be welded without subsequent heat-treatment.

In the ammonia-soda industry, stainless steel is commonly specified for the construction of the CO_2 compressor valves, valve seats, piston rods, etc., and for the construction of centrifugal pump rods, steam turbine blades, etc.

Aluminum is slowly attacked by strong ammoniated brine, and its use is confined to plain brine or weak sodium carbonate solutions.

Even cast iron is attacked by hot ammoniated brine or hot gases containing ammonia, carbon dioxide, and steam, but its corrosion rate is slower than that of steel. Actually there is no metal or alloy of metal that is absolutely unattacked by this combination of materials at elevated temperatures; it is a matter only of the relative lengths of life and the cost of the materials that determine their fitness.

Except in the gas system, where, if there are any valves at all, globe valves with hard-rubber seating rings are used, the entire liquor system is equipped with cast-iron cocks, ground metal-to-metal or packed inside with vulcanized asbestos packing. Lubricated cocks are very serviceable. They give tight service against corrosive liquors, and their plugs are easier to turn.

Impellers of centrifugal pumps made of cast iron are frequently pitted or eaten up by the hot ammoniated brine or hot filter liquor. So also are the cast-iron cocks.

Ammoniated brine or other hot ammonia liquors are also very corrosive in their effect on the packing material and pipe joints. Packings for centrifugal and plunger pumps must be of a lead-graphite-asbestos composition or of a very soft metallic material. Flange gaskets are cut from 1/16- to 1/32-in. pure rubber sheets.

Process.—The raw materials are brine, limestone, and ammonia. Limestone is burned to supply carbon dioxide for soda ash and brine for the recovery of the ammonia. The carefully purified brine is pumped to a head tank from which it flows to the cast-iron absorber tower. Here it is saturated with ammonia. Some carbon dioxide is likewise absorbed.

The brine leaves the bottom of the tower, is settled and then cooled. The cooled solution is pumped to the top of the carbonator, a cast-iron tower. Carbon dioxide from the kiln is compressed and cooled and then sent to the bottom of the carbonator. The resulting suspension of sodium bicarbonate in an ammonium chloride solution is filtered on a rotary drum filter. The washed sodium bicarbonate drops onto a belt conveyor which feeds the furnaces. Here the bicarbonate is decomposed by calcination into soda ash, carbon dioxide, and water. The ash then passes through a rotary cooler and goes to concrete silos. It can be either shipped or converted into caustic soda.

SODIUM CHLORATE

The Second World War brought with it greatly increased production of chlorates in this country. Batch processes have given way to continuous processes. Other improvements in production technique have followed.

Production

Materials of Construction.—The equipment used by the U.S. Department of Agriculture (Groggins, P. H., *et al.*, Electrochemical Production of Sodium Chlorate, *Chem. & Met. Eng.*, Vol. 44, No. 6, pp. 302–307, 1937, and Vol. 45, No. 12, pp. 692–696, 1938) included cells of black-iron plate. The upper section of the cell was protected on the inside by asbestos cement. Covers were impregnated insulating asbestos board. Glass-lined steel vessels were used for settling cell liquors. The sand filter was a covered steel vessel. The suspension of salt in hot chlorate liquor was delivered to a cast-iron vessel. The salt was deposited on a Monel screw. To ensure a colorless product, the hot chlorate liquor was cooled and crystallized in a glass-lined vessel.

Commercial plants for the production of sodium chlorate used a brick-lined tank for dissolving the raw materials and for the sump tank. Feed tanks may be Tygon-lined steel. The electrolytic cell is steel with mild-steel cathodes and graphite anodes. The filter, too, is Tygon-lined steel. The chlorate crystallizer is made of nickel. The centrifuge is nickel and stainless steel. Piping is generally glass, chemical stoneware, chemical porcelain, or high-silicon iron.

Process.—The process for making sodium chlorate at the Los Angeles plant of Western Electrochemical Co. has been described. See Potassium Perchlorate.

SODIUM CHLORIDE

Salt is one of the most widely occurring chemical substances in nature and one of the most corrosive. It gives trouble in sea water, in which it occurs in about a 3 per cent solution, in various other concentrations in water and other solvents, and in the solid form.

Salt is refined by any one of several processes. The three that will be discussed here are the grainer pan, vacuum pan, and Alberger.

Production

Materials of Construction.—Formerly it was customary to use iron and steel for much of the equipment. More recently the trend has been toward using Monel, Ni-Resist, Worthite, Durimet 20, high-silicon iron, and other special alloys. This has come about through realization of the savings to be made by use of corrosion-resistant materials of construction and by the desire for cleanliness and purity of food products.

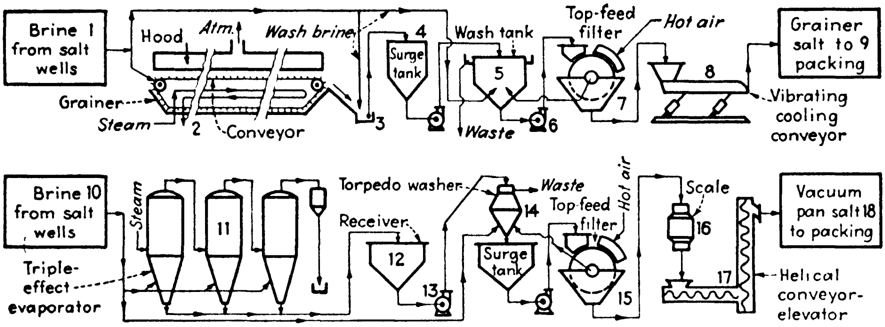
Grainer-pan Process.—In the grainer process the purified and filtered brine is pumped from white pine settling tanks or iron, which are sometimes protected with nonmetallic coatings, by Worthite pumps to grainer pans. The long shallow pans are constructed of steel, Monel, wood, or concrete. The brine is heated by steam pipes of cast iron or steel. As the salt is crystallized, it is brought to the front end by a steel or Monel rake and pushed into a Monel launder or trough. The salt slurry is conveyed by gravity or on a rubber belt to a surge tank and is pumped by Worthite or Ni-Resist pumps to a tank in which the salt crystals are washed. The salt slurry is piped through plain steel, cast iron, or Monel to a rotary vacuum filter and dryer. It is equipped with a Monel or stainless-steel hood, filter cloth, and winding wire. The dried crystals are passed over a Monel vibrating cooling conveyor. Following this the lumps are crushed or removed, and the grains of salt sorted for the trade. Cylindrical wire-mesh screens, shaking screens, or bolters are used. Frequently Monel wire cloth is employed, although some plants prefer steel. The salt grains of various sizes are deflected by Monel distribution pipe to Monel or steel hoppers and thence to maple-lined bins. All parts of the weighing and packaging machinery which come in contact with the salt are constructed of Monel.

Vacuum-pan Process.—In the vacuum process the purified brine is evaporated in a multiple-effect evaporator of welded steel (may be cement-lined) or cast-iron body, steel tube sheets, and copper, steel, or Monel tubes. Vapor lines are steel. Circulation is increased by the use of impellers of Ni-Resist.

Salt is drawn continuously from the evaporator in a slurry through the salt leg. The feed brine is introduced into the bottom of the leg, so that the salt is washed by the incoming brine. The slurry is pumped by a Worthite or cast-iron pump with Worthite or Ni-Resist impeller. Some plants use a Monel shaft and fittings. It goes to a rotary vacuum filter for dewatering and drying. The filter is equipped with a Monel screen and Ni-Resist grids. The dried salt leaving the filter is ready for screening and packaging.

Piping in a salt plant is plain steel and cast iron or, where greater purity is demanded, Monel metal.

Some plants use another device for separating the salt crystals from the brine. A steel, bronze, or Monel receiver and a continuous centrifuge with Monel baskets are used, in which case Monel hoppers and chutes are used to carry the wet salt from the conveyors to the centrifugals. The latter are equipped with Monel spreading belts. Where receivers and centrifugals are used, the product goes directly to dryers in Monel screw conveyors, in a Monel-lined wood trough, or on belt conveyors. The dryer is a rotary drum through which the salt passes slowly. Monel or nickel-clad steel is used in almost all dryers for the flights and linings.

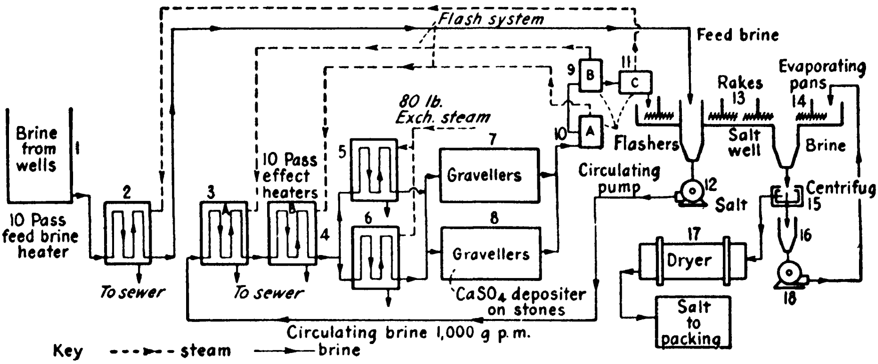


Salt processes (Grainer-pan system above and vacuum-pan system below).

1. White pine, nickel-clad steel, steel
2. Steel, Monel, wood, concrete
3. Monel
4. Steel, Monel
5. Monel
6. Worthite, Monel, Ni-Resist
7. Monel
8. Monel
9. Monel, steel
10. White pine, steel, nickel-clad steel
11. Steel, cast iron; tubes of copper, Monel, steel, plain or cement-lined
12. Steel, Monel
13. Worthite, Monel, Ni-Resist
14. Steel, Monel
15. Monel
16. Monel with stainless pivot
17. Monel, steel
18. Monel, steel

Alberger Process.—An Alberger unit consists of brine heaters, a calcium sulphate-removal system, flashers, and open evaporating pans. The evaporation of brine is carried out in what might be called a "closed" system by circulating brine through the equipment continuously. All the brine which enters the suction of the circulating pump, except about 7 per cent which is evaporated during the cycle, passes through the entire system of heaters, gravelers, flashers, and open pans and finds its way again to the suction of the pump—where feed brine is added to replace that lost by evaporation.

Starting at this point, the first step in the process is that of heating. As the brine leaves the circulating pump and passes through the series of heaters, its temperature is raised to about 290°F. From the heaters, the brine is passed through a cylindrical vessel filled with stones, which is the "graveler." Here the brine deposits calcium sulphate.



Alberger salt process.

1. Steel
2. Monel shell, tube sheets, and baffles; Monel-clad heads; admiralty brass, Cu 80, Ni 20, Monel tubes
3. Monel shell, tube sheets and baffles; Monel-clad heads; admiralty brass, Cu 80, Ni 20, Monel tubes
4. Monel shell, tube sheets, and baffles; Monel-clad heads; admiralty brass, Cu 80, Ni 20, Monel tubes
5. Steel shell, tube sheets, and baffles; low-nickel-steel tubes
6. Steel shell, tube sheets, and baffles; low-nickel-steel tubes
7. Steel
8. Steel
9. Steel
10. Steel
11. Stainless steel
12. Stainless-steel casing and impeller
13. Ni-Resist spiders, Monel rakes
14. Steel bottom and salt well, Monel sides; anodized aluminum hood (not shown)
15. Tobin bronze or Monel basket; Monel sieve and backing screen
16. Monel
17. Monel-clad steel shell, Monel flights
18. Ni-Resist steel casing, Monel impeller

It then goes to the flashers, where evaporation begins. The pressure on the brine is released in three flashers in series, and each drop in pressure brings about flash evaporation and an accompanying drop in temperature. In the third flasher the pressure is dropped to approximately atmospheric, and it is here that salt begins to crystallize.

The mixture of salt and brine is discharged at the boiling point through a pipe extending beneath the surface of the brine in an open pan. Here surface evaporation and further crystallization occur, and finally the brine overflows from the pan and passes again to the suction of the circulating pump. The salt is drawn from the pan to a centrifuge from which it passes to a Monel-clad rotary dryer.

Multiple-effect evaporation is obtained by using the vapor from the first two flashers to heat the circulating brine in corresponding heaters and by using a portion of the vapor from the third flasher to heat the feed brine.

High-silicon iron pumps and valves have been used to handle saturated salt brine at temperatures as high as 280°F. in the production of NaCl. Durimet 20 also is successfully applied in this same service.

Handling

Iron and Steel.—Cast iron and carbon steel are widely used throughout industry for pumps, valves, tanks, and piping handling natural brine, sea water, and relatively pure sodium chloride solutions. Corrosion generally occurs; however, its rate can usually be kept low enough to make their use practical if iron contamination is not objectionable. Careful design and installation of piping and equipment used for salt solutions, brines, and sea water are important. Corrosion in such systems is accelerated by contact of dissimilar metals, by dissolved air, by stray electrical currents, and by excessive velocities and turbulence.

In addition to consideration of the design features noted, chemical control is generally used to reduce corrosion in refrigerating brines. This can be accomplished in closed systems by adding an inhibitor, such as sodium dichromate, and adjusting the pH to a value between 8 and 9. For open systems disodium phosphate is recommended with a pH between 7.5 and 8.

Correct design, supplemented by the use of inhibitors and pH control, has been found to reduce corrosion in brine systems as much as 95 per cent. (Spitz, A. W., Iron and Steel, *Chem. Eng.*, Vol. 54, No. 10, p. 211, 1947.)

Worthite.—An outstanding economical application for Worthite pumps and valves is in the handling of hot salt slurries in salt refineries. The salt slurry from the evaporator pan carries about 50 per cent salt crystals at an average temperature of 160°F. This slurry is pumped to vacuum filters or separators, and Worthite pumps have given 8 years' service to date without requiring any repairs. Pump stuffing boxes are sealed with water seals, and packing lasts about 9 months.

Cold brine solutions are handled in both all-iron and standard fitted pumps with relatively good service records. However, in the salt refinery where returns from the separator carrying 3 per cent crystals mix with the evaporator feed, and where the temperature is a little higher, there is some corrosion. Bronze impellers last longer than cast iron, as the soft graphitized surface formed on a cast-iron impeller is worn off by the high-velocity brine carrying a small amount of crystals. However, the galvanic action of bronze (impellers and rings) on the cast-iron casing has been known to perforate the casing in 3 to 4 years. Worthite impellers and rings in such pumps will last indefinitely, and there is no noticeable galvanic action with the cast-iron casing.

The lack of galvanic action between cast iron and Worthite has led to the use of Worthite internal parts in many pumps handling sea water, harbor water, and brackish river or well water. Worthite is preferable to the ordinary stainless steels, as the galvanic action with cast iron is less and Worthite does not pit in sea water during shutdown periods as do many of the stainless steels.

Oil-field brines are notoriously corrosive, and large numbers of Worthite pumps are used for transfer service to collecting ponds and for pumping through pressure filters prior to injecting the salt water back into the ground. High-pressure Worthite centrifugal pumps and Worthite liners in reciprocating pumps are used in the injection service. (Pratt, W. E., Worthite, *Chem. Eng.*, Vol. 54, No. 10, p. 211, 1947.)

High-silicon Irons.—These have been successfully used as materials of construction for many years in applications involving sodium chloride solutions as the corrosive medium. The excellent corrosion-resistant properties of these alloys apply for solutions at all concentrations and temperatures.

The molybdenum-containing alloy Durichlor is usually preferred in sodium chloride services, but the added cost of 3 per cent molybdenum sometimes limits its use where Duriron will give satisfactory results. Duriron may give comparable results in relatively pure brines. However, where appreciable amounts of such contaminants as chlorine (or other halogen gases) or hydrochloric acid are present, the Durichlor alloy gives superior service. (Luce, W. A., High-Silicon Irons, *Chem. Eng.*, Vol. 54, No. 11, p. 217, 1947.)

Carbon and Graphite.—These materials are unattacked by salt, either dry or in aqueous solution at all temperatures. Karbate impervious carbon and graphite products are equally inert and can be used up to their normal operating-temperature limitation of 340°F.

The most extensive use of carbon products in contact with brine is in the universal use of graphite anodes in caustic-chlorine cells. A second and similar application is the use of graphite anodes in cathodic protection systems for condensers and pipe lines in sea-water and salt-marsh conditions.

The principal use of Karbate products in contact with brine solutions is for those involving heat-transfer equipment of all descriptions, including concentric, bayonet, cascade, and shell and tube types. The fact that Karbate equipment is unattacked either by clean sea water or by salt water contaminated with industrial wastes as found in inlets makes it almost universally applicable for cooling operations using sea water as the cooling medium. (Werking, L. C., Carbon, Graphite, *Chem. Eng.*, Vol. 54, No. 11, p. 218, 1947.)

Nickel and Alloys.—Monel, nickel, Inconel, and the Ni-Resist alloys have a high degree of resistance to sodium chloride and brine solutions under practically all conditions of concentration, temperature, and aeration. Monel, nickel, and Ni-Resist are being used for a great many applications in the production of salt and in its utilization in such processes as soap manufacture, caustic soda and chlorine production, food brining, and refrigeration.

Nickel or nickel-clad steel is used for such equipment as salt-dissolving and brine-storage tanks, soap lye treating and storage tanks, evaporator tubes and coils in such industries as soap, caustic, and food processing. The Ni-Resist austenitic cast nickel-iron alloys are used for such equipment as pump casings and impellers, valves and cast pipe handling brines and for bodies and plates of filter presses and rotary salt filters. Type 1 Ni-Resist (Ni, 14; Cu, 6) and Type 2 Ni-Resist (20 per cent Ni) generally are used for brine service except where the parts are subject to severe thermal shock. Under such conditions, the relatively high expansion coefficient of these two types may possibly make them subject to cracking, and the use of Type 3 Ni-Resist (30 per cent Ni), having low expansion coefficient, is desirable. For example, in a filter press handling spent soap lye at 175°F. and washed out with cold water after each filtration, it was found that Type 3 Ni-Resist was required for filter plates for this reason.

Inconel may occasionally be subject to localized attack or pitting in hot chloride solutions under low-velocity conditions. Such attack, when it does occur, usually is shallow and nonprogressive, and serious pitting is not common.

Monel, nickel, Inconel, and the Ni-Resist alloys are usefully resistant to corrosion by sea water. With Monel, nickel, and Inconel, conditions of relatively high velocity are most favorable. In stagnant exposure the accumulation of marine organisms may induce pitting of these materials. Monel is used for such equipment as sea-water pumps, rods, and valves; boat propeller shafts; and a wide variety of marine fittings. Ni-Resist is used for pumps, valves, piping, and other equipment where a cast material is required.

None of these is subject to stress-corrosion cracking in chloride solutions. (Friend, W. Z., Nickel, Nickel Alloys, *Chem. Eng.*, Vol. 54, No. 12, p. 225, 1947.)

Rubber.—Sodium chloride has very little effect on either natural or synthetic rubber and can be handled by either soft or hard linings. Selection of type of lining will be dependent upon service conditions, principally upon operating temperatures.

At high temperatures, heat aging of the lining is the important factor, and the best service life is obtained from specially compounded ebonite compounds. Concentrated solutions of sodium chloride can be successfully handled with compounds of this type at temperatures up to 220°F. Satisfactory commercial installations have been made in crystallization tanks operating at temperatures up to this maximum.

Rubber-covered agitator equipment has also been supplied. Rubber-lined pipe and fittings have been successfully used for recirculation of brines in chlorine production. (True, O. S., Rubber Linings, *Chem. Eng.*, Vol. 54, No. 12, p. 228, 1947.)

Lead.—Excellent service records are characteristic of metallic lead products when used to resist corrosion by salt-water, spray, or seaside atmospheres. There is some corrosion of lead from sodium chloride, but this is so slight that years of useful life are obtained from lead pipe, valves, boat keels, sinkers, and sheet lead in various forms. The last serves as tank linings, protective roofing, caps for wood piling, and a host of other uses where the low corrosion rate of lead means a long life of protective service.

Lead shows only slight corrosion (4 to 5 mils per year) when exposed to 1*N* sodium chloride and practically no corrosion when exposed to salt spray. Corrosion resistance of lead to salt water is well illustrated by the wide use of lead pipe in handling sea-water supplies to aquariums throughout the country. (Church, H. M., Jr., Lead, *Chem. Eng.*, Vol. 54, No. 12, p. 230, 1947.)

Silver.—Silver is recommended as a material of construction exposed to the corrosive influence of sodium chloride solutions where high purity of the solution has to be maintained. Silver-clad material can be used where solid-silver construction is too expensive. Great progress has been made in the production of electrolytic silver coatings free from pinholes.

Silver exposed to boiling sodium chloride solution loses approximately 0.14 mil per year increasing to approximately 2.8 mils per year if sodium chloride solution is aerated.

Molten sodium chloride attacks silver rapidly. (Rosenblatt, E. F., Precious Metals, *Chem. Eng.*, Vol. 54, No. 12, p. 232, 1947.)

Chemical Stoneware.—Chemical-stoneware piping and pumps can be used for handling brine solutions, and at least one installation of stoneware for handling chlorinated brine from chlorine cells is known. An interesting application, where absolutely no iron contamination is allowable, is in the pumping of sea water to aquariums. It may be said in summation that, although chemical stoneware is admirably suited to the handling of sodium chloride brines, it is not widely used because other equipment is more readily available and in some cases more economical. Thus chemical stoneware is reserved for the stringent applications which no other equipment will bear. (Herstein, F. E., Chemical Stoneware, *Chem. Eng.*, Vol. 55, No. 1, p. 223, 1948.)

Haveg.—Haveg equipment is completely resistant to chemical attack from sodium chloride in all concentrations and within the temperature limitations which have been established for this plastic material.

Aeration of brine solutions or the presence of hydrochloric or similar nonoxidizing acids is not detrimental. Furthermore, the presence of other chlorides, such as calcium, zinc, magnesium, or ferric chloride, either individually or collectively, will not institute attack, as occurs in the cases of cast iron, steel, and many ferrous alloys. Haveg fabricated into such articles as pumps, valves, pipes, fittings, storage tanks, and dissolving tanks has given excellent service for years in such brine applications. Its use on a larger scale has been restricted primarily by economic considerations but, where justified, has resulted in low amortization and maintenance costs. (Mampe, E. P., Haveg, *Chem. Eng.*, Vol. 55, No. 1, p. 223, 1948.)

Durimet and Chlorimet.—Experience has shown Durimet 20 to be a satisfactory material of construction for applications involving various sodium chloride solutions. As is the case with iron-base alloys and especially the high-chromium stainless steels, which depend on an oxide film for their corrosion resistance, the Durimet alloy occasionally gives indications of the pitting type of corrosion.

Durimet 20 will remain resistant to clean, aerated sea water but will pit when subjected to the varied oxygen-concentration conditions initiated in dirty, unaerated sea water.

Similar reasoning can be applied to industrial sodium chloride solutions (brines). However, in these cases the oxygen supply is generally uniform throughout the system. Although this alloy was found to be susceptible to pitting attack under unaerated conditions, many industrial applications have been found in which it can be successfully applied. A few of these applications are as follows:

A production process in a soap plant involves recirculation and build-up of sodium chloride at temperatures up to 180°F. Durimet 20 gate valves are used extensively, and they are giving very good service.

In the production of commercial salt, Durimet equipment is showing excellent service for saturated salt brines at temperatures up to 280°F.

The high-silicon irons are often preferred over Durimet because of their lower cost and better corrosion resistance. However, many applications require the use of machinable alloys, and it is generally for these conditions that Durimet 20 is used when applicable. Valves are often made with high-silicon iron plugs and Durimet bodies. (Luce, W. A., Durimet, Chlorimet, *Chem. Eng.*, Vol. 55, No. 1, p. 223, 1948.)

Aluminum.—Sodium chloride both in the solid form and as brines has been satisfactorily handled in aluminum equipment. Even in contaminated solutions the total amount of attack on aluminum is small. However, when certain contaminants are present, *e.g.*, compounds of heavy metals such as copper, nickel, and lead, the total amount of attack, though small, may be highly localized. If such dangerous contaminants are encountered, the corrosion hazard can be greatly minimized by the use of equipment fabricated from a duplex product known as "Alclad."

Because chloride solutions are especially effective in promoting galvanic corrosion of aluminum, equipment to handle sodium chloride solutions should be designed to avoid contact of dissimilar metals. For example, contact between aluminum and copper fixtures should be avoided. However, in many instances it is possible to protect aluminum cathodically in the presence of steel by the use of zinc- or aluminum-alloy attachments.

The high resistance of aluminum alloys to saline exposures has been demonstrated by the many applications in conditions where equipment has been subjected to sea water. Aluminum alloys such as 2S, 3S, 52S, and 63S are virtually unaffected by unpolluted sea water. Although very little difference exists in resistance to corrosion of these metals, 52S has been particularly outstanding in its resistance to marine conditions. If the water is polluted by industrial wastes, Alclad metals are recommended because they are especially resistant to localized failure.

Brines, especially when inhibited, have been used successfully in refrigeration systems fabricated of aluminum alloys. Oil-well brines are being handled in aluminum piping.

Since compounds of aluminum are usually colorless or white, traces of the harmless metal leave the color of the product or refined salt unaltered. Aluminum has been used for mining- and drying-machinery structural materials in mines and other miscellaneous equipment. The preliminary processing equipment, such as hoppers, elevator buckets and shafts, as well as drying towers, is all composed of aluminum. Wooden shipping containers for salt are lined with aluminum sheet to prevent the egress of salt and the ingress of moisture. (Balash, J. P., Aluminum, *Chem. Eng.*, Vol. 55, No. 1, p. 224, 1948.)

Hastelloy.—Experience with the corrosion resistance of Hastelloys A, B, and C to sodium chloride has been limited, in general, to sea-water applications. These alloys have been subjected to both spray and immersion tests.

Test samples of cast and of sheet alloy in all three grades were subjected to flowing sea water at a depth of 3 to 4 ft. in a channel which conducted sea water into a chemical plant on the Atlantic Coast. Velocity of flow in the channel averaged 1 to 2 ft. per sec. Cast and sheet forms of Hastelloy A and B showed generally uniform corrosion with some shallow pitting after 1,834 days. The depth of pit varied between 0.015 and 0.023 in. Of all alloys tested, alloy C was the most resistant. Cast, sheet, and welded-sheet samples, as well as samples of cast pipe and welded tubing, all had an excellent to perfect appearance after 1,837 days of exposure, with no weight loss and no pitting.

An unusual application of alloy C involves its use in heat exchangers installed in a large chemical plant. The tubes carry aluminum chloride and hydrochloric acid. Salt water as a coolant is pumped into the jacket surrounding the tubes. Whereas the jacket would normally be fabricated of carbon steel for fresh-water service, in this case alloy C was used to resist corrosion from the salt water. (Chisholm, C. G., *Chem. Eng.*, Vol. 55, No. 1, p. 288, 1948.)

Stainless Steels.—Chromium-nickel types of stainless steel are resistant to sodium chloride solutions of practically all concentrations and temperatures, provided that a neutral or alkaline condition is maintained. Boiling solutions generally can be handled successfully unless the metal is in a stressed condition. The stainless steels usually are not satisfactory for prolonged contact with slurries or supersaturated solutions of sodium chloride. Although freshly prepared sodium chloride solutions are neutral, hydrolysis during stagnation establishes an acid condition which will induce localized attack on stainless steel. Of all the stainless-steel grades, Type 316 is most resistant to this kind of corrosion.

Types 316 and 317, the modified stainless-steel grades containing molybdenum, are more resistant than the other stainless-steel grades to the attack by pitting which is characteristic of mediums containing sodium chloride. While Types 316 and 317 are subject to attack resulting from surface contamination, from prolonged contact with moist sodium chloride crystals, or from slightly acid solutions of sodium chloride such as stagnant sea water, such hazardous conditions of exposure often can be eliminated by careful planning. Where the exposure conditions are severe, the service life of the metal can be extended by proper cleaning during and after use. In special cases where the exposure time is short or where the corrosive medium is very mild, the regular chromium-nickel grades may be suitable.

The corrosion resistance of stainless steel is highly desirable in the food-processing and meat industries, where sodium chloride and various brines and sauces containing salt are used for processing, preserving, or flavoring. Kettles for mixing and cooking, tanks for blanching, troughs, molds, trays, tables, trucks, chutes, and conveyors are made of Type 304 or Type 316, depending upon the service condition. Slicers and packaging equipment for hams and bacon containing salt also are made of Type 316. Stainless-steel thermometers are inserted in hams to observe temperatures during processing.

Type 316 resists the corrosive action of many, but not all, food-flavoring sauces and brines for pickles. Most of the usual pickling solutions containing salt, vinegar, and sugar can be handled safely, and the equipment can be kept in good condition by flushing occasionally with water.

The Type 304 pumps, piping, and valves provide excellent service in refrigeration circulating systems for salt brines which are controlled to maintain constant alkalinity. Vats, rolls, and other apparatus used for tanning and dyeing withstand the action of alkaline solutions containing sodium chloride at boiling temperatures. In the production of soap, the "salting out" operation is carried out in stainless-steel Type 316 vessels.

Tanks and vessels of stainless steel resist attack by some sodium chloride-acid solutions used for metal cleaning, food processing, and various other purposes. For example, certain solutions containing water, sodium chloride, sulphuric acid, and nitric acid are not harmful. The corrosive action of such solutions, of course, varies with the concentrations of the ingredients as well as the solution temperature.

In the petroleum industry, Type 316 oil-well tubing and housings for pumps are useful where brines are associated with the crude oil.

Corrosive effects resulting from the direct exposure of the stainless steels to sea water may depend upon additional factors. In all cases, Type 316 offers superior corrosion resistance. In actual service tests, Type 316 has remained unattacked during 5 years of immersion in fresh sea water. However, surface contamination over long time intervals by marine organisms and the hydrolysis of the salt to create an acid condition in stagnant water can promote localized attack. Types 304 and 316 stainless-steel equipment such as fishing lures, hooks, small boats, propellers, and linings in ship holds which can be rinsed occasionally to remove salt deposits or cleaned to dislodge organisms will provide satisfactory service. Storage tanks in which sea water is held stagnant are subject to attack if hydrolysis has occurred, but any of the chromium-nickel grades can be used if the water is maintained at pH 8 to 9 by the addition of sodium hydroxide. (Snair, G. L., Jr., Stainless Steels, *Chem. Eng.*, Vol. 55, No. 1, p. 230, 1948.)

Protective Coatings.—Most of the work that has been done on the use of protective coatings in the presence of sodium chloride or sodium chloride brines has been done in connection with exposure to sea-water conditions. The information secured in sea water is not necessarily applicable to problems involving the handling of sodium chloride solutions that are relatively sterile. The living organic life in sea water has a deleterious effect on many organic coatings. Most paint film materials have fairly good resistance to sodium chloride solutions, and the main difficulty in trying to protect equipment against fog or solutions containing sodium chloride is the penetration of the film and subsequent corrosion and rusting of the parent metal. The oleoresinous varnishes, with either a drying oil plus a natural resin or a synthetic resin, have good resistance. Spar varnish has been widely used, and the chlorinated rubber-base varnishes have been quite successful. Most of the plastic-base paints have good resistance to sodium chloride solutions, including the phenol-formaldehyde resins, the melamine-formaldehydes, the urea-formaldehydes, the polyvinyl chlorides, the vinyls, and the alkyds. Some of the tar-base paints have shown excellent resistance to sodium chloride brine.

Brine-storage tanks or any other equipment in constant contact with sodium chloride brine must have a very good surface preparation. It is usually desirable to use a suitable primer and enough coats of the material chosen so that there will not be penetration of the film by the brine or water vapor. The baked-on coatings have been more successful than the air-dried coatings. (Anon., Protective Coatings, *Chem. Eng.*, Vol. 54, No. 12, p. 226, 1947.)

SODIUM DIPHENYL SULPHONATE

In some cases plastic pipe has not proved to be so satisfactory as other materials. In an installation in the Dow Chemical Co.'s plant, a gravity line carrying sodium diphenyl sulphonate was made up of 120 ft. of 2-in. pipe. Since this product forms a coating on the inside surface of any material used for the pipe line, the line must be cleaned with steam about once a month. Saran, however, did not stand up to more than five or six cleanings and had to be replaced after 6 months with copper pipe which, though it may not be so chemically resistant, will probably last longer under these particular conditions. (Williams, D. R., Saran Pipe, *Chem. & Met. Eng.*, Vol. 52, No. 11, pp. 112–113, 1945.)

SODIUM HYDROXIDE

Sodium hydroxide is made by either of two processes: (1) the electrolytic and (2) the chemical. In the first any one of several electrolytic cells produces both caustic soda and chlorine. In the latter method sodium carbonate is treated with lime to form sodium hydroxide. Most of it is made at ammonia-soda plants.

Production

Materials of Construction.—Caustic soda can be processed and handled in ordinary cast iron and steel below 70 per cent strength under 200°F. Above 200°F. embrittlement may occur. However, when an iron-free product of high purity is required, such as in the case of the rayon industry, it is essential to use special materials of construction. Nickel and the nickel alloys are generally used. In concentrations above 70 to 75 per cent caustic soda, nickel is second only to silver in resisting corrosion. Silver equipment is used for making and handling chemically pure caustic.

Electrolytic Process.—Brine is brought to the plant in cast-iron pipe lines, while rock salt is delivered by rail and stored in concrete tanks. The salt is dissolved in concrete, rubber- or brick-lined steel tanks. At a German plant raw brine was stored in outdoor tanks made of steel lined with Oppanol (polyisobutylene) protected on the inside by a course of acidproof brick.

Tanks where brine is treated for precipitation of soluble magnesium and calcium sulphates are usually plain steel or rubber- or brick-lined steel. It is reported that a German plant filtered the resultant slurry through polyvinyl cloth on wooden frames while another filtered brine on its way to cell feed tanks through a paper medium. The paper had been in use since cotton became critical and had proved to be more satisfactory than cotton both in life and in lower turbidity of the brine.

The temperature of the purified brine is raised in steel heat exchangers and the solution saturated with salt. It is then reheated to prevent salt precipitation in the distribution mains. The warm saturated brine goes to the cells through hard-rubber lines and enters the cells through tantalum orifices.

In the case of the diaphragm cells steel tanks with concrete or soapstone covers are used. To reduce the weight of covers, asbestos fibers can be added to the mix. Steel is used in the form of wire-mesh screen or perforated sheet for the cathode. The anode is graphite treated with linseed oil or other impregnating material. In mercury cells, rubber-lined steel tanks are used. Most of the bottom is left unlined so that the electric contact with the mercury cathode can be established. The cover is rubber-lined steel, although sandstone was formerly employed. Natural rubber is said to have a longer life than GR-S.

Chlorine goes to the chlorine department, and as a rule the hydrogen is permitted to escape into the atmosphere. The weak caustic soda is piped to steel storage tanks and from there to evaporators. These consist of bodies fabricated from nickel-clad steel or lined with nickel sheets or, for low concentration, 3 per cent nickel cast iron. The steam chests are made from nickel, downtakes are nickel or nickel-clad steel, and tubes are nickel. The evaporators are equipped with high-velocity nickel or 30 per cent nickel, Ni-Resist, or Monel circulating pumps.

Although considerations of product purity have been most important in determining the choice of nickel for evaporators, users have reported that nickel has been sufficiently more desirable than steel to justify its use entirely on the basis of economy.

The development of nickel-clad steel has made possible the construction of evaporators having all exposed surfaces of pure nickel and at the same time low enough in cost to permit their extensive use.

The discharge, containing 30 to 50 per cent caustic, passes to a nickel-clad settler or filter with a nickel screen, where salt is removed. It can be shipped at this concentration or further concentrated. In the latter case the 50 per cent solution is pumped to a steel storage tank. It is then pumped to another evaporator and concentrated to 73 to 75 per cent. This evaporator is all-nickel construction. As required, it is withdrawn and pumped to plain cast-iron pots and concentrated to anhydrous. The concentrated mass while hot can be pumped to steel drums or over a steel chilled flaking wheel. The flaked caustic can be crushed, screened, and packed into packages of various size flakes.

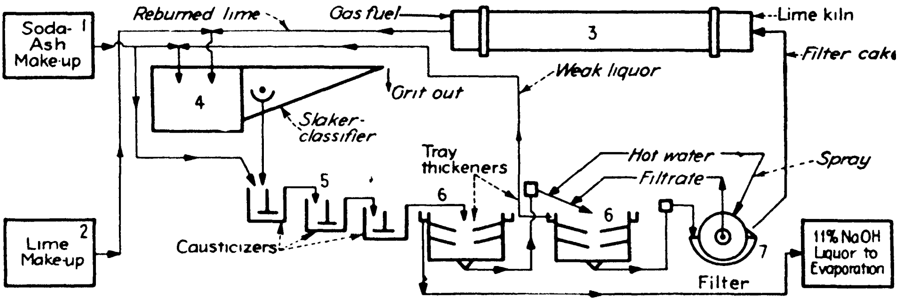
Caustic for the rayon industry requires special treatment in special metallic equipment. In this case the 30 per cent caustic is pumped to a crystallizer. The body is generally nickel-clad or nickel-sheet-lined steel. Shafts and agitators are nickel or Monel. The slurry passes to a centrifuge with nickel basket and wire-cloth liner for removal of the salt.

The caustic solution is then pumped by nickel, iron, Durimet 20, Worthite, or Ni-Resist pumps to an evaporator, where it is concentrated to 50 per cent. This solution can be shipped to the rayon consumer in nickel-clad or -lined containers.

When iron-free solid caustic is required, it is concentrated in nickel cast-iron pots and flaked in equipment with nickel surfaces except for the cast Ni-Resist cooling drum.

It is reported that a German plant used cast-iron pots of 11-ton capacity for producing anhydrous caustic. These pots were said to be unique in that they had strong, tight-fitting tops and were operated at a finishing temperature near 440°C. at a vacuum of 360 mm. Hg. Since adopting vacuum operation, pot life had been increased from 100 to 250 charges per pot. Some of the newer pots were installed in a fully suspended, dutch-oven type of setting which also made for much longer pot life. In the United States large-tube vertical evaporators of all-nickel construction are used for the same purpose.

Lime-soda Process.—In this process the caustic soda is made from sodium carbonate produced by the ammonia-soda process. Plain cast iron and steel are used throughout, as caustic below 50 per cent concentration can be handled without corrosion difficulties.



Caustic soda (lime-soda process).

1. Steel
2. Steel
3. Brick lined
4. Steel
5. Steel
6. Steel
7. Steel

In many small plants the soda solution from storage tanks is causticized in large flat-bottom tanks. Steam is used to heat the liquor. Lime is added to a steel perforated basket attached to the side and partially submerged in the liquor. Several such tanks are used in rotation. Decantation of the supernatant caustic solution is carried out through a swing pipe. The liquor is allowed to settle, and the clear portion containing 10 per cent caustic is drawn off through the swing pipe. The lime sludge is then washed to recover the remaining caustic. (How, T. P., "Manufacture of Soda," 2d ed., p. 287, Reinhold Publishing Corporation.)

A more up-to-date practice that gives a stronger caustic and requires less wash water is the Dorr system of continuous causticizing agitators and thickeners.

The weak caustic made by either method can be evaporated by standard methods described under the production of caustic by the electrolytic process.

Handling

Nickel.—Where the possibility of metallic contamination is important, particularly to users of caustic in the rayon, soap, and photographic-film industries, nickel and nickel alloys are used. Nickel confers on its alloys a high degree of resistance to corrosion by caustic solutions. For example, Monel, containing two-thirds nickel, has resistance to corrosion by caustic of the same order as that of nickel. Similarly, moderate additions of nickel to cast iron or steel greatly improve the resistance to corrosion by caustic alkalis.

Nickel and Monel in hot concentrated (30 to 70 per cent) caustic solutions have consistently low corrosion rates. In concentrations above 70 to 75 per cent caustic soda, nickel is second only to silver in resisting corrosion.

Inconel is usually best for alkaline sulphur solutions such as hot concentrated sodium sulphide solution. However, under conditions of exposure such as those associated with pump impellers, nickel has been found to be most satisfactory because of its better retention of protective films. In the absence of sulphur, nickel forms a protective oxide and is second only to silver in resisting fused caustic. However, the presence of sulphur in fused caustic, as in "shading" operations, makes the use of nickel impractical for caustic pots.

Inconel is being used in fused caustic applications, but it seems to have a slight effect on the color of the product due to the formation of chromates. Consequently, it is not generally used by companies making solid caustic to sell but principally by those engaged in carrying out caustic fusions where either higher mechanical properties at elevated temperatures are required or resistance to sulphidizing conditions above 600°F.

In one instance Inconel is being satisfactorily used for heater tubes evaporating caustic from 75 to 95 to 98 per cent at atmospheric pressure where the tubes are internally fired with manufactured-gas flame. The use of Inconel is preferred for these heater tubes because of the high internal temperature and because of the fact that L nickel is subject to intergranular attack when sulphur compounds are present in the gases of combustion above 600°F. Inconel is resistant to such sulphur embrittlement by oxidizing sulphur compounds at temperatures up to 1500°F.

The beneficial effect of nickel additions to the corrosion resistance of cast iron in moderately concentrated caustic is considerable. The nickel contents of 20 to 30 per cent provide very marked improvement as compared with unalloyed cast iron. As low as 3 to 5 per cent nickel nearly doubles the corrosion resistance of cast iron.

Cast Iron and Steel.—These materials are widely used for processing and handling caustic below 70 per cent strength under 200°F. Above that temperature embrittlement may occur. However, plain iron and steel will rust if the exposure to caustic is interrupted by periods of exposure to air, water, or neutral solutions. Furthermore, hot concentrated solutions corrode iron rapidly enough to contaminate the caustic seriously.

For bulk storage of 50°Bé. caustic, mild-steel tanks are used. The caustic is generally transferred with mild-steel pumps. Plain carbon steel is also used for diluting from 50 to 26°Bé. This metal is used for most tanks, pumps, and pipe in handling caustic.

Some engineers prefer to protect the exteriors of steel vats containing caustic solutions with a bituminous enamel.

An engineer in a plant handling 50 per cent caustic reports that carbon steel is used for storage tanks and that this material works well as long as a good quality steel is obtainable and the tank is built with a wall thickness of ¾ in. However, steel in thin sections is not satisfactory because caustic embrittlement produces a network of hairline cracks in the tank wall. He states that they might patch up one tank where embrittlement has done its work by welding a sheet of stainless steel over the section which was cracked and leaking but this was not satisfactory. So for small, thin-walled tanks he uses nickel-clad steel or 302 stainless steel.

Graphite.—Impervious graphite heaters are used to prevent metallic contamination of 50 per cent caustic. The heater was designed for a maximum temperature of 300°F. on the tube side. (Ford, C. E., *Chem. Eng.*, Vol. 54, No. 1, p. 94, 1947.)

Teflon.—This material has given excellent service in a number of valve applications. Solid rings have been used as valve stem packings for caustic in all concentrations up to 375°F. Present indications are that the packing will last as long as the valve, with no replacement required.

Teflon seating disks have been used in globe valves and needle valves with excellent results, since they resist erosion as well as corrosion. One of the conditions under which these valves have operated is caustic soda of 21 per cent at 250°F.

Saran.—For siphons and short pipe lines one manufacturer handling caustic employs Saran tubing. He reports that the chemical resistance of Saran appears to be good enough to permit him to use it in moving caustic solutions hot and up to 40 per cent concentration. The only trouble is that it becomes brittle at elevated temperatures.

Packaging

Rayon-quality caustic soda has been transported in ships whose holds have been lined with nickel.

Tank cars for transporting caustic are of various types. Some cars are lined with brushed neoprene for 70 per cent caustic, which is loaded at 200°F. Internally nickel-plated tank cars have been used. (Friend, W. Z., *Ind. Eng. Chem.*, Vol. 39, No. 10, p. 1229, 1947.) Nickel-lined or -clad tank cars are used for shipping 75 per cent caustic.

SODIUM HYPOCHLORITE

Materials of construction play an important part in both the manufacture and distribution of sodium hypochlorite.

Production

Materials of Construction.—In manufacturing concentrated sodium hypochlorite, the presence of even traces of iron are objectionable, since iron compounds have been found to effect a decomposition of such solutions. Accordingly, iron is to be avoided whenever possible in the manufacturing process. (Baker, J. H., Sodium Hypochlorite, *Chem. & Met. Eng.*, Vol. 41, No. 10, p. 530, 1934.)

Concrete-lined wood tanks are sometimes used to make up chlorine solutions and for the storage of sodium and calcium hypochlorite. For mixing and settling, concrete tanks with steel and cast-iron agitator parts are in use. An engineer writes that, from his experience over a period of years, concrete reaction and filter tanks, when properly constructed, give the best all-round service. Prufcoat has been used satisfactorily as a protective coating over concrete in sodium hypochlorite solutions.

Rubber-lined tanks are suitable if extreme care is used to bond the rubber lining to the steel. If, however, when applying the lining, the workman allows even a few pinholes to penetrate it, the solution passing through these openings attacks the metal, setting up a gas pressure between the lining and the tank which has a tendency to force the lining from the metal. This results in contamination and subsequent decomposition of the liquor.

Rubber-lined steel pumps, piping, valves, fittings, and reaction vessels have been used. Hard-rubber piping, valves, and fittings also have been used. Stoneware cooling coils have found wide use in manufacture of sodium hypochlorite. (Herstein, F. E., *Ind. Eng. Chem.*, Vol. 39, No. 10, p. 1254, 1947.) Cylindrical stoneware tanks are used to a considerable extent for small plants making sodium hypochlorite bleach for local consumption.

Lead pipe is used to introduce chlorine gas or liquid into a bath of caustic in a concrete tank in the production of the hypochlorite. High-silicon iron pumps are extensively used.

Process.—Sodium hypochlorite is made commercially by the reaction of liquid or gaseous chlorine in a solution of caustic soda.

High-silicon iron and Durichlor are both being applied as pumps, valves, tank outlets, coolers, pipe, and ejectors in the production and use of sodium hypochlorite. Both alloys show good resistance in solutions up to 15 per cent available chlorine, with Durichlor normally being used above the 15 per cent concentration.

Handling

Rubber-lined tanks, pipes, and fittings of natural or synthetic material are successfully used.

Worthite pumps are used with excellent results for alkaline bleach solutions (sodium and calcium hypochlorite) as commonly used for bleaching textiles and paper. Recommendations for Worthite are sodium hypochlorite, cold, 3 per cent maximum available chlorine; calcium hypochlorite, cold, 3½ per cent maximum available chlorine. Worthite is not recommended for use in the manufacture of these hypochlorites in the concentrated form involving 15 to 23 per cent available chlorine.

Stainless steels, Types 316 and 317, have been used successfully for handling alkaline sodium hypochlorite solutions containing 0.3 per cent available chlorine in equipment for entire bleaching cycles.

Nickel, Monel, and Inconel are frequently resistant in alkaline chlorine solutions, such as the sodium or calcium hypochlorite solutions used for bleaching and sterilizing purposes, where available chlorine concentrations are as high as 3 g. per l., in discontinuous operations, such as cyclic textile bleaching, where the bleaching cycle is followed by rinsing and acid "scouring" in the same vessel. In higher concentrations, attack is likely to be severe and accompanied by pitting. These materials are resistant to continuous exposure to the very dilute hypochlorite solutions, usually containing less than 500 ppm. available chlorine, used for sterilizing purposes. In the washing of hypochlorite-bleached paper stock, Monel is used for wire covers and other parts of vacuum washers and for lining the vats and repulper sections of these washers.

Hastelloy C is resistant to strong sodium and calcium hypochlorite solutions.

Saran-lined steel pipe is being used for 12 per cent sodium hypochlorite at 60 to 70 lb. pressure at 100°F.

Durimet 20 resistance depends·on many variables. It is usually satisfactory. Normally this alloy is satisfactory up to a few per cent available chlorine at usual temperatures. However, high-silicon iron and Durichlor are so much more satisfactory that they almost completely exclude the use of Durimet 20 or similar stainless steels.

Chlorimet 3 pumps, valves, and miscellaneous equipment are being used for bleach solutions in both make-up and handling.

Karbate can handle a solution up to 25 per cent concentration and up to the boiling point.

Glass tanks are in use for handling a 16 per cent solution.

SODIUM HYPOCHLORITE—HYDROCHLORIC ACID

The entire equipment at the American Enka Corp.'s rayon plant for handling the mixture of sodium hypochlorite and hydrochloric acid, centrifugal pumps, piping, valves, and storage tanks, is made of chemical stoneware. (Kingsbury, P. C., Storage of Corrosive Liquids, *Trans. A.I.Ch.E.*, Vol. 23, p. 90, 1929.)

SODIUM ISOAMYL ETHYL BARBITURATE

Amylal is dissolved in absolute alcohol in a glass-lined tank. (*Glass Lining*, Vol. 11, No. 3, p. 15.) A 50 per cent solution of caustic soda is added here, and the pH carefully adjusted. The solution is then transferred by gravity to a suction filter. The two-stage steam ejectors with condensers supply the vacuum for filtering. The filtering is done in a stoneware filter, and the solution then run into a glass-lined, steam-jacketed still in which it is concentrated.

SODIUM METABISULPHITE

Sodium metabisulphite or its water solution can be handled satisfactorily in stainless steel of Type 347, 316, or 304 or in Monel, lead, lead-lined steel, rubber-lined steel, copper, or wood. Stainless-steel equipment should be annealed after welding. (E. I. du Pont de Nemours & Co., "Materials Handling for Groundwood Bleaching with Solozone," Wilmington, Del.)

SODIUM NITRATE

Natural sodium nitrate is found in several places. The important deposits are located in Chile and are known as "caliche." The other constituent of the ore is sodium chloride. Sodium nitrate also is made synthetically.

Production

Materials of Construction.—The dissolving tank in the Shanks process is usually steel and in the Guggenheim process, concrete. Evaporators have steel shells, charcoal-iron tubes, and cast-iron valves. Filter cloth is Monel. Crystallizers and tanks are made of steel. Piping is steel. Pumps are either iron or steel. Valves and fittings are brass or cast iron. The latter should be trimmed with 12 per cent chrome steel or 18-8 chrome-nickel steel. For the production of synthetic nitrate of soda, nitric acid absorption towers are made of chrome-nickel stainless steel.

Guggenheim Process.—The ore is crushed and separated into fine and coarse material. (Badger, W. L., and E. M. Baker, "Inorganic Chemical Technology," 2d ed., pp. 77–79, McGraw-Hill Book Company, Inc., New York, 1941.) The fine material is mixed with mother liquor, filtered on a Moore filter, and washed with weak liquor. Filtrate and wash water result in a solution of sodium nitrate returned to the main cycle.

Coarse ore is leached in large concrete tanks. Mother liquor at 40°C. is circulated through four such tanks in series in countercurrent (the strongest liquor is taken from the tank that has been just charged, and the weakest liquor is fed to the tank that is most nearly exhausted). The warm strong liquor is passed through a series of tubular heat exchangers, which reduce its temperature to 15°C., and is then cooled by ammonia refrigerating coils to 5°C. It then goes to a thickener which separates the crystals, and the cold liquor is returned through the series of heat interchangers to go back to the leaching system.

The slurry of crystals that is recovered from the bottom of the thickener is centrifuged, dried, and briquetted. These briquettes are melted in a direct-fired furnace, and the fused sodium nitrate is pumped through spray nozzles to give a final product that consists of pellets of a uniform size.

Handling

Both plain cast iron and steel can be used for handling sodium nitrate solutions. Pumps can be all-cast iron or 18-8 Cb stainless steel.

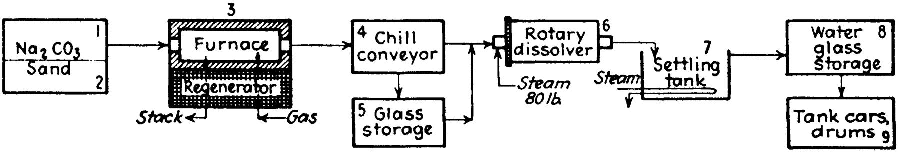
Ingot iron is said to be more resistant than plain iron to molten nitrates. In some plants nickel-clad steel vessels with L-nickel-sheathed heating elements are used for fused sodium nitrate heat-treating baths.

SODIUM SILICATE

There is little trouble involved in either the production or handling of sodium silicate.

Handling

Sodium silicate can be stored in either steel or reinforced concrete tanks. Weigh tanks of steel are satisfactory. Pipe and fittings of steel are used. Valves can be all-iron; pumps cast iron or steel with medium-length square braided flax packing.



Sodium silicate.

1. Steel
2. Concrete
3. Fire brick
4. Neoprene
5. Concrete, wood, steel
6. Steel
7. Steel
8. Steel
9. Steel

Pipe and fittings: valves, all iron; pump, cast iron, steel; packing, flax

Solid sodium silicate, known as "sodium silicate glass" or simply "glass," can be handled in wood, steel, concrete, or other ordinary materials.

Neoprene is being used for a conveyor belt handling hot sodium silicate sinter. (Bridgwater, E. R., Neoprene as a Construction Material for the Chemical Industry, *Trans. A.I.Ch.E.*, Vol. 35, p. 445, 1939.)

Packaging

Sodium silicate is shipped in steel drums and tank cars.

SODIUM SULPHATE

Sodium sulphate is also known as "salt cake" or "glauber's salt" depending on the purity.

Production

Materials of Construction.—For a discussion of the materials used in making salt cake from sulphuric acid and salt see Hydrochloric Acid on page 176. In the manufacture of glauber's salt from the impure material, lead equipment is most often used.

It has been reported (Worthington Pump & Machinery Corp., *Bull.* W-350B6) that in the Texas Panhandle plants are using Worthite pumps for handling slurries of natural salt cake. Warm water is forced down through the salt beds below the surface, and the saturated brine is pumped to the refinery, where it is evaporated, refined, and crystallized. These operations require the handling of hot brine solutions carrying very high percentages of salt crystals in suspension. Worthite pumps and valves have proved to be a satisfactory answer to a once troublesome and costly maintenance problem.

When sodium sulphate is by-product in the production of sodium and potassium chromates and bichromates, an interesting corrosion problem is present. (Corrosion Forum, *Chem. & Met. Eng.*, Vol. 52, No. 3, p. 174, 1945.) Before purification sodium sulphate is in saturation solution, and about 0.3 per cent of bichromate is present as an impurity. Pumps, tanks, and pipes handling this solution last 5 to 6 years. They are made of plain carbon steel. The bichromate impurity is removed by reducing it with sulphur dioxide gas in a ceramic-filled tower. After reduction and precipitation as hydrate, the chrome is removed by filtration in an iron Kelly press.

Once the bichromate, which never amounted to more than 1 per cent of the sodium sulphate solution, is completely removed, the solution becomes too corrosive to be handled in plain carbon steel, that is, if it is desired to produce glauber's salt which is not contaminated with iron. The evaporator, therefore, is made of Monel. Copper, which would seem satisfactory from a chemical point of view, is not used because the evaporator is a forced-circulation type and at the high velocity the sharp sodium sulphate crystals would erode it. The centrifuges and dryers which follow the evaporator in the process are lined with Monel or 18-8 stainless steel, and here again carbon steel might be used except that a pure product is required. Furthermore, it was found that in the case of expensive equipment like evaporators, centrifuges, and dryers it is more economical to stand the higher first cost of the alloy than to replace periodically the same pieces of equipment made of ordinary carbon steel.

An engineer reports that he has successfully used cast-iron pumps, galvanized-iron or wooden crystallizing pans, steel tanks, and wooden filter presses in producing sodium sulphate.

Salt-cake Process.—For a description of the process for making salt cake from sulphuric acid and salt see Hydrochloric Acid on page 176.

Hargreaves Process.—Here is another method for producing sodium sulphate. (Shreve, R. N., "The Chemical Process Industries," 1st ed., McGraw-Hill Book Company, Inc., New York, 1945.) It is carried out by passing sulphur dioxide and air from a furnace over prepared salt lumps in vertical steel chambers with false bottoms. Several of these chambers are run in series, and the gas is moved countercurrently. The complete cycle for the reaction, cleaning, and repacking, is 3 days for each individual chamber.

Three-stage Process.—Anhydrous sodium sulphate from lake crystals has been described. (Pierce, J. B., Jr., Dehydration of Natural Occurring Sodium Sulphate Crystals, *Trans. A.I.Ch.E.*, Vol. 34, pp. 153–164, 1938.)

Glauber's Salt Process.—It is made by dissolving salt cake in mother liquor, removing impurities, clarifying, and crystallizing. (Shreve, *loc. cit.*) The salt cake is dissolved in large, circular, lead-lined wooden tanks. The solution is then treated with a paste of lime followed by milk of lime in sufficient quantities to neutralize the solution. Stirring is carried out by a paddle, and heating by a lead pipe running to the bottom. Precipitated impurities of iron, magnesium, and calcium are allowed to settle, and the clear solution is run to crystallizers by side outlets. The precipitated mud is washed with water, and the water is used as make-up for the process. Crystallization is carried out in pans lined with lead. When the solution cools to temperature, the pan is drained and the crystals are collected and centrifuged.

Handling

At boiling temperature a 10 per cent solution can be handled in plain iron or lead. Copper is also satisfactory. An aqueous solution of salt cake is handled by an all-bronze, all-cast iron, or 18-8 Cb stainless pump. Durimet pumps give satisfactory service handling molten sodium sulphate at 500°F.

Packaging

Salt cake is shipped in barrels and in box cars. Glauber's salt is packed for shipment in bags and in wooden barrels and kegs.

SODIUM SULPHATE—SODIUM CHLORIDE—SULPHURIC ACID

Chlorimet 2 shows good resistance to handling a reactor dump solution at 240 to 250°F. It is composed of 28 per cent sulphuric acid, 28 per cent sodium sulphate, 3 per cent sodium chloride, a small amount of methyl alcohol plus 30 per cent water. (Luce, W. A., *Chem. Eng.*, Vol. 55, No. 8, p. 224, 1948.)

SODIUM SULPHHYDRATE

When making barium chloride from barite and coal in a kiln, a black ash, barium sulphide, is formed. (White, E. D., Barium Chemicals Production, *Chem. Eng.*, Vol. 56, No. 1, pp. 90–93, 1949.) This is leached with water and steam. The slurry is pumped to a steel tank lined with acidproof brick and cement.

Here it is treated with hydrochloric acid pumped in by a high-silicon iron pump. Very pure hydrogen sulphide is liberated. This gas is conducted into a steel absorbing tank, where it reacts with sodium sulphide solution to form sodium sulphhydrate. Once the H_2S content has been adjusted, the solution from the absorber is pumped to storage for packaging and shipment.

SODIUM SULPHIDE

This chemical is not particularly severe on materials of construction, especially if some small amount of contamination is not objectionable, as is sometimes the case.

Production

Materials of Construction.—Such equipment as cast-iron reaction kettles, pumps, and filter presses are used extensively in production. (Rother, W. H., Utilizing Cast Iron in Chemical Equipment, *Chem. & Met. Eng.*, Vol. 40, No. 7, p. 350, 1933.) However, the stainless steels, nickel, and Monel and a few other special materials are also used.

A nickel-clad-steel evaporator is in use for concentrating sodium sulphide from 3 to 30 per cent. The vapor body is fabricated from 20 per cent nickel-clad steel. The steam chest is equipped with seamless nickel tubes. The same applies for evaporators concentrating from 30 to 60 per cent solution. Nickel pumps, piping, and valves are used to circulate sodium sulphide liquors between the evaporator effects. One company uses an Inconel evaporator.

Process.—Three methods are used for making sodium sulphide. The most used is the reduction of sodium sulphate with powdered coal in a reverberatory furnace. A second process is the reduction of barite in the same manner, leaching, and double decomposition with soda ash. The third method involves the saturation of a caustic soda solution with hydrogen sulphide and the addition of another equal portion of caustic soda. The reaction must be carried out above 850°C. (White and White, Manufacture of Sodium Sulphide, *Ind. Eng. Chem.*, Vol. 28, p. 244, 1936.) Specially designed small reverberatory furnaces seem to give the least difficulty because they avoid overheating the charge. The reaction takes place in a liquid phase and is very rapid. Rotary kilns of the type used for calcining limestone have been applied with some success to this reaction. The reduction of barium sulphate takes place very similarly. The black ash coming from the furnace is run into iron tanks and allowed to cool. This crude sulphide can be dissolved hot; after settling, it can be run into shallow crystallizing tanks, where colorless crystals separate out. A more concentrated sulphide can be obtained by evaporating the liquor at 160°C. in a cast-iron pot. The molten hot sulphide is then pumped into ordinary caustic soda drums for shipping.

The concentration can be handled somewhat differently. (White, E. D., Barium Chemical Production, *Chem. Eng.*, Vol. 56, No. 1, pp. 90–93, 1949.) The sodium sulphide liquor is fed from storage, after prolonged settling, in the evaporation system. Concentration is carried out in two stages. In the first, using steam at 100 psi., a concentration of 30 per cent is reached. The second is accomplished using direct heat in gas-fired nickel-clad-steel fusion pots. The final product contains 60 to 62 per cent Na_2S and has a boiling point of 183°C. This solution is settled and pumped to a storage tank which feeds a conventional type of Monel flaker. It is converted to flaked form and packed for shipment.

Handling

Sodium sulphide solutions up to 70 per cent concentration and at temperatures up to and including the boiling point have been handled by E. I. du Pont de Nemours & Co. in cast iron and steel, but corrosion is sufficient to result in considerable iron pickup in the product and in certain items, such as pumps, to involve excessive maintenance. The more concentrated solutions are more corrosive, and attack is accelerated by increase in temperature. (West, J. R., "Corrosion of Constructional Materials by Sulphur and Sulphides," p. 55, Texas Gulf Sulphur Co. Industrial Fellowship, 1946.) Extensive laboratory tests indicated that Monel and nickel form a thin adherent coating or film providing adequate protection and are satisfactory for these conditions. Under static conditions Inconel showed up fairly well, but adherence of the coating was less satisfactory. H. L. Maxwell of Du Pont in a letter to West, from which the above experience was taken, also wrote that stainless steels were less resistant and carbon steel and cast iron showed rates of attack up to 0.001 in. per month.

A solution of 50 per cent sodium sulphide at 200°F. attacked stainless steel Type 410 to the extent of 0.00055 in. per month and stainless steel Type 304 not at all, and both were corroded by condensation products. (Letter to West from Allegheny Ludlum Steel Corp.)

A solution of sodium sulphide was evaporated under vacuum to dryness over a period of 21 hr., the maximum temperature being 200°C. Stainless steel Types 430 and 304 were corroded at the rates of 0.06 and 0.05 in. per year, respectively. (S. W. Shepard of Calco Chemical Division reported to West.)

Type 310 stainless steel is being used very successfully for resistance to sulphide solution, particularly where contamination of the product by iron would be serious. (Letter from B. E. Field of Union Carbide & Carbon Research Laboratory to West.)

Nickel pumps are used to handle hot concentrated solution.

Lead is used successfully with these solutions at temperatures up to 100°C.

Packaging

Sodium sulphide can be shipped in ordinary steel.

SODIUM SULPHITE

Sodium sulphite has many applications, *e.g.*, as an antichlor after bleaching, for bleaching textiles, in photographic developing baths, as a general reducing agent because of its available content of sulphur dioxide and others.

Production

Materials of Construction.—A lead-lined wooden vessel is used for the reactor. Natural-rubber filter presses and stainless-steel equipment are also used.

Process.—The most important commercial procedure for this compound is the passing of sulphur dioxide into a solution of soda ash until the product has an acid reaction. (Shreve, R. N., "The Chemical Process Industries," 1st ed., p. 264, McGraw-Hill Book Company, Inc., New York, 1945.) At this point the solution consists chiefly of sodium bisulphite. This can be converted into sodium sulphite by adding more soda ash to the solution and boiling until all the carbon dioxide is evolved. The reaction is carried out in a large lead-lined wooden vessel. After the solution has settled, it is concentrated, whereupon crystals settle out on cooling.

Another commercial source of this material in the crude anhydrous form is from the preparation of phenol by the fusion of sodium benzene sulphonate with sodium hydroxide. (Groggins, P. H., "Unit Processes in Organic Synthesis," 2d ed., p. 628, McGraw-Hill Book Company, Inc., New York, 1938.)

One firm reports that in its plant a 30 per cent solution is brought to boiling (214°F.) in an atmospheric evaporator, then cooled to 90°F. The evaporator is Type 317 stainless-clad steel. Coils carry steam and brine alternately and are made of the same type of stainless steel. The solution is filtered before it reaches the evaporator by a natural-rubber plate-and-frame press. Rubber lasts one year and is doing a satisfactory job. The company does not feel justified in a large capital outlay for a stainless-steel press, a material which would probably last indefinitely.

Handling

Lead and Monel are used successfully with solutions up to 20 per cent concentration at 25°C.

An aqueous solution can be handled by an all-bronze, 18-8 Cb, stabilized 18-8 Mo, or higher chrome-nickel stainless-steel or lead pump. Redwood has also been found to resist solutions of the salt satisfactorily.

Sodium sulphite is not usually handled in plain iron or steel.

Packaging

This chemical compound can be packed in paper-lined wooden kegs or barrels, multiwall paper bags, and fiber drums.

SORBITOL

Sorbitol is a hexahydric alcohol made by the reaction of corn sugar with hydrogen. Until recently it was made by electrolytic reduction of corn sugar. Atlas Powder Co. has announced a high-pressure catalytic hydrogenation process which is now in operation at the Atlas Point, Del., plant.

Production

Materials of Construction.—Prior to demineralization, all equipment in the sorbitol process is constructed of ordinary steel, since there is negligible corrosion and contamination is slight and of no consequence. The ion-exchange unit is made of rubber-lined steel to resist corrosion and contamination. All equipment after this step is made of stainless or stainless-clad steel to ensure maximum purity of the product.

Process.—Converting corn sugar to sorbitol takes place in five main steps: (1) preparation of feed slurry by dissolving sugar in water and mixing with special catalyst, (2) continuous high-pressure catalytic reduction of glucose to sorbitol in a specially designed reactor, (3) separation of spent catalyst from clear sorbitol solution by filtration, (4) purification by deionization followed by decolorization with activated carbon, (5) concentration by evaporation of the purified solution followed by adjusting the final concentration to exactly 70 per cent sorbitol through addition of demineralized water in agitated weigh tanks. (Porter, R. W., Sorbitol from Corn Sugar by Catalytic Reduction, *Chem. Eng.*, Vol. 54, No. 11, pp. 114–117, 1947.)

The first step in the process is to make up a sugar-water sirup. Sugar and warm water come together in the dissolving tank. The solution is pumped to a large tank which provides storage capacity to feed the continuous reactor. Catalyst is discharged directly into a weighed quantity of sugar solution. Resultant slurry is pumped to a storage or surge tank in the autoclave building.

The slurry of sugar solution and catalyst is pumped from the surge tank into the continuous reactor. Hydrogen is bubbled into the reactor, which is several vertical tubes. Reacted slurry and excess hydrogen discharge to a receiver where hydrogen is separated from the slurry.

Sorbitol solution is separated from spent catalyst in a pressure leaf filter. The clear filtrate solution passes to intermediate storage. The crude sorbitol must be purified. Ionizable salts are removed in a two-stage ion-exchange unit using organic ion exchangers.

After demineralization, the solution is pumped to a tank where it is mixed with a prepared slurry of activated carbon. Organic impurities and color bodies are absorbed by the carbon, after which the slurry is filtered on a plate-and-frame filter press. The purified water-white sorbitol solution is pumped to storage tanks prior to being concentrated by evaporation.

A stainless-steel single-effect continuous evaporator is used to concentrate the solution from below 50 per cent sorbitol to slightly higher than 70 per cent. The evaporator discharges continuously into agitated blending tanks.

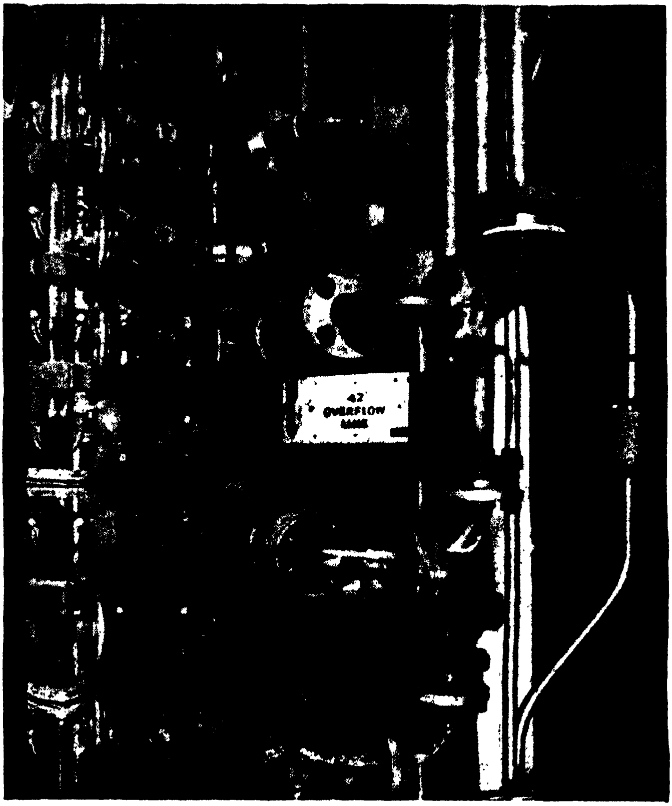
Pure 70 per cent sorbitol solution ready for shipping is stored in stainless-steel tanks from which it is drawn to fill 50-gal. drums or tank cars.

SOUPS

Stainless steels are used for such applications as reservoir tanks in making soups. These overhead tanks feed soup from cooking kettles above into the canning machines. Stainless-steel soup buckets used in connection with the canning are also found in such plants. This metal has given satisfactory service for many years.

In the processing of soups aluminum cookers and steam-jacketed kettles are used to prepare many kinds of soup.

Nickel kettles have been in use in the preparation of a great variety of soups in the plants of several manufacturers. (LaQue, F. L., Nickel and Its Alloys, *Food Ind.*, Vol. 7, No. 12, pp. 580–582, 1935.) Nickel soup trucks, soup-blending equipment, etc., are also used.



A manifolding header showing a combination of Pyrex glass and Type 316 stainless-steel piping, using ferrule joints. The Pyrex pipe is used here for visibility. The joints are covered with lead shields for safety against sudden leaks.

SOYBEAN OIL

Operations must be carried out in equipment fabricated only from those materials which experience has shown to be free from any tendencies toward contaminating the oil with traces of certain metals. (Goss, W. H., Modern Practice in Solvent Extraction, *Chem. & Met. Eng.*, Vol. 48, No. 4, pp. 80–84, 1941.) The presence of minute amounts of copper, as well as numerous other metals, is fatal to the stability of refined soybean oil. In edible-oil production the corrosion problems incident to the choice of a solvent and materials of construction revolve not around damage to the equipment but rather around the damage caused by metallic contamination of the product.

For further information see Vegetable Oils.

SPICES

In the continuous extraction of natural spices in dry soluble form stainless-steel heat exchangers, percolators, distillation assemblies, and refrigerating units are used.

STANNOUS PHENOL SULPHATE

Stannous phenol sulphate is recovered from rinsing tanks in the acid bath of tin plating. It is concentrated in evaporators and returned to the plating bath. Nickel is essential for these evaporators because of its high corrosion-resisting properties that in addition to giving long service life also prevent metallic contamination of the recovered bath. (*P.I.Q.*, Vol. 7, No. 4, p. 5, International Nickel Co.) The evaporator bodies and heater shells are nickel-clad steel equipped with Monel tube bundles. Miscellaneous tubing, pipe, fittings, and valves are also Monel and nickel.

STREPTOMYCIN .

Proper selection of construction materials for equipment was one of the most important phases of design in the Elkton, Va., plant for the production of streptomycin of Merck & Co. (Porter, R. W., Streptomycin Engineered into Commercial Production, *Chem. Eng.*, Vol. 53, No. 10, pp. 94–98, 1946.) This was necessary not only from the standpoint of equipment corrosion but, perhaps more important, to prevent contamination of the product.

Production

Materials of Construction.—Although plain carbon steel is satisfactory for many processing operations, stainless steel is generally used. Stainless steel is used for pipes, fittings, valves, pumps, tanks, filters, evaporators, and other process equipment. Much of the equipment at the finishing plant is made of stainless steel. Rubber-lined tanks; porcelain piping, valves, and fittings; Hastelloy filters; and Durichlor pumps are used in the elution process. Rubber-covered pump impellers are used to combat erosion from carbon slurries. Glass-lined steel is employed in the final extraction process. Aluminum is used for absorption tanks, supplementary tanks, acetone storage tanks, piping, and fittings.

Process.—Original mash for fermentation consists of a dilute solution containing glucose, peptane, meat extract, and salt. After being pumped to the fermenter, the mash is sterilized. It is inoculated and fermented. Fermentation temperature is controlled by cooling water in coils or jackets.

The fermenter charge containing large amounts of mycelium is pumped to an agitated surge tank from which it is drawn off continuously. Here begins the recovery of the traces of streptomycin.

Separation of streptomycin from the liquids is carried out in a continuous pressure-type filter using a filter aid both as a precoat and as an admixture in the broth. After filtration the pH of the filtrate is adjusted before passing through a second filter for final polishing. Filter cake is discarded.

Clear broth is mixed with activated carbon which adsorbs streptomycin. It is filtered on a pressure filter, and the carbon adsorbate cake is washed with alcohol to remove impurities. The slurry is refiltered, and the filtrate containing the solvent returned to the recovery plant. Adsorption takes place continuously. Streptomycin is removed from the carbon in a two-stage countercurrent elution process using acidified solvent. Streptomycin hydrochloride is formed here in solution.

As previously stated equipment for elution is comprised of rubber-lined or glass-lined elution tanks, porcelain pipe and fittings, Durichlor pumps, and Hastelloy and rubber-lined filters.

Rich acid eluate is neutralized and concentrated by use of a single-pass evaporator. The dilute aqueous solvent solution of streptomycin hydrochloride passes through a series of three evaporators.

Streptomycin in the concentrate is precipitated by addition of another solvent. The precipitate of crude streptomycin is retained on a plate-and-frame filter press. The crude cake is dried in a vacuum dryer. It is temporarily stored in drums.

After being redissolved in a solvent, the crude material passes through a continuous process. Finally, the purified streptomycin is precipitated, filtered, and dried in a vacuum dryer. This material is then redissolved to form a concentrated solution which is treated to remove pyrogens. Then it is passed through a biological filter and placed in stainless-steel containers for shipment to the finishing plant at Rahway, N.J.

The containers of streptomycin solution are received in a specially designed, sterile building. It is here that the operations of blending, final bacterial filtration, freezing, drying by high-vacuum sublimation, milling, weighing into vials, and packaging are carried out under conditions to ensure sterility of the final product.

Packaging

Packaging is done in glass vials.

STYRENE

This chemical is used mostly in making polystyrene and synthetic rubber. It can be made by any one of several processes. The most important for synthesizing styrene consists of treating benzene with ethylene in the vapor phase in the presence of suitable catalysts to give ethylbenzene. This, in turn, is catalytically dehydrogenated to styrene at high temperatures in the presence of suitable catalysts. Styrene can also be obtained by cracking isopropylbenzene. In another process, styrene is one of the resultant products when crude oil is cracked by spraying against hot refractory brick. Some is also obtained as a by-product of the water-gas industry. (Reinhart, F. W., Substituted Styrenes Modify Polymer Properties, *Chem. Ind.*, Vol. 62, No. 8, pp. 235–237, 1948.)

Production

Materials of Construction.—The ethylbenzene section of the Los Angeles plant operated by Dow Chemical Co. contains no corrosion-resistant alloys but relies on the maintenance of anhydrous conditions to enable the handling of hydrocarbons containing hydrogen chloride in mild-steel equipment. Hydrogen chloride has been shown to be necessary as a promoter in the aluminum chloride catalyzed reaction. (Smith, H. H., Los Angeles Styrene Plant, *Chem. Eng. Progress,* Vol. 43, No. 4, p. 152, 1948.)

In the styrene section, 18-8 stainless steel and 5 per cent chrome steels are used in the dehydrogenation plant where temperature conditions demand them, and mild steel throughout the remainder of the system. (*Ibid.*)

The I.G. Farben. plant at Schkopau used a glass-lined steel reactor for the ethylene-benzene reaction. All parts in contact with the hot reaction mixture were either glass-lined or coated with a baked-on phenolic resin. The separators and coolers were phenolic resin-lined. The water wash and separation equipment was glass-lined, while the caustic wash and subsequent separation was carried out in iron and steel. [Boundy, R. H., and R. L. Hasche, Manufacturing of Thermoplastics in Plants of I.G. Farben., Report 1069, Combined Intelligence Objectives Committee, G-2 Division, SHAEF (Rear) APO 413, U.S. Department of Commerce.]

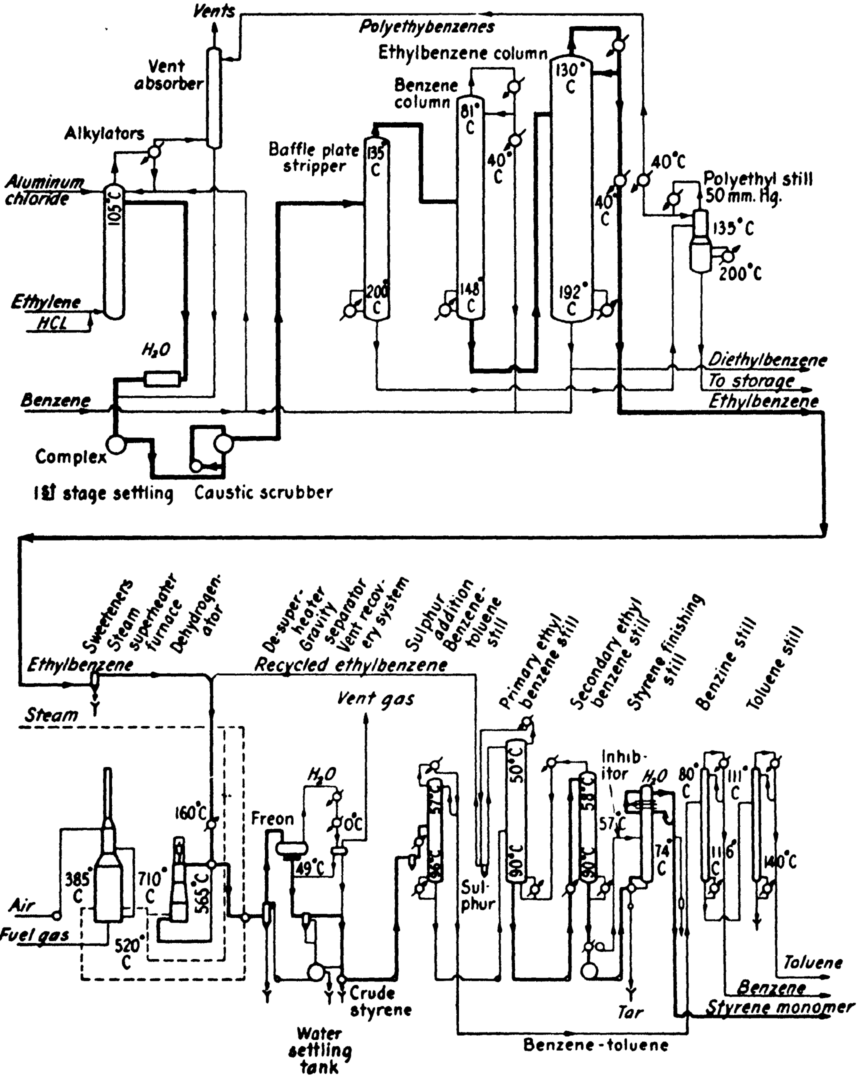
In the dehydrogenation plant at Schkopau the furnace tubes were 18-8 stainless steel. Tubes and all parts of the furnace exposed to reactants were lined with a copper alloy (containing 3 per cent Mn) to prevent carbon formation.

Distillation equipment included aluminum storage tanks, tin-lined stills and condensers, and iron piping.

In some plants Inconel steam superheaters are used to heat steam to 1500°F. for reaction with ethylbenzene to make styrene.

Ethylbenzene Process.—Benzene and ethylene are combined in the reactors in the presence of aluminum chloride. The alkylation product is a mixture which is washed and then fed to a train of steel distillation towers. (Smith, H. H., Los Angeles Styrene Plant, *Chem. Eng. Progress*, Vol. 43, No. 4, p. 152, 1948.) Benzene is returned to the reactor, and ethylbenzene is taken overhead from the ethylbenzene still and sent to the styrene system. Diethylbenzenes are withdrawn from the bottom of this column for return to the reactor. Granular aluminum chloride is fed continuously to the reactor by means of a variable-speed screw conveyor.

In the styrene section of the process two hydrocarbons are removed from ethylbenzene to form styrene. Ethylbenzene is vaporized, flows countercurrent to the cracked product vapors through a heat exchanger, and enters the base of the reactor.



Styrene. In ethylbenzene section maintenance of anhydrous condition enables handling of hydrocarbons containing hydrogen chloride in mild steel. In styrene section 18-8 stainless steel and 5 per cent chrome steel are used in dehydrogenation plant where temperature conditions demand them, and mild steel throughout remainder of system.

Steam is superheated to 710°C. before entering the reactor with the ethylbenzene vapors. The reaction takes place at 625°C. Coming out of the reactor, the product vapors are heat-exchanged and then condensed to give oil and water phases.

Noncondensed gases from the main condensers are compressed and cooled in the recovery system. The wet hydrocarbons are added to the crude styrene, and the by-product hydrogen is used as fuel.

Steam serves two purposes in the reaction: to reduce the vapor pressure of hydrogen and to carry heat in the endothermic dehydrogenation reaction.

Purification is accomplished by subatmospheric distillation in a train of continuous stills. The first tower removes an overhead stream of benzene and toluene, which are formed in the dehydrogenation reaction, and these materials are purified in two columns.

Styrene is finished in a modified batch still to a purity of 99.5 per cent.

Handling

Styrene can be handled and stored in plain steel or other commonly used materials of construction.

SUGAR

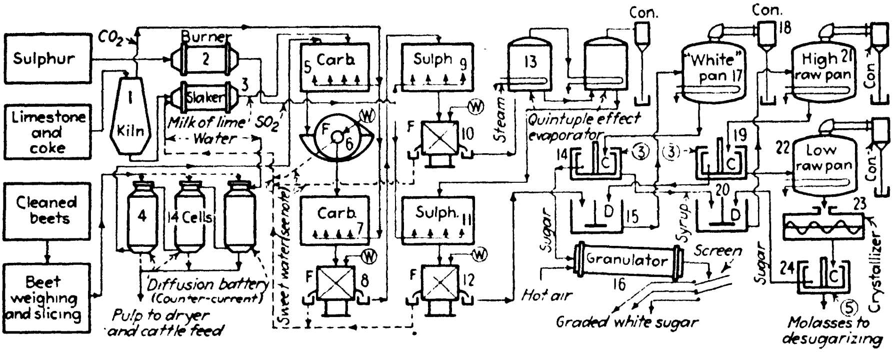
Operations involved in the recovery and purification of sugar from cane consists (1) of making the raw sugar and (2) of refining the raw sugar. In both steps, most of the equipment is fabricated from mild steel but some special materials such as copper and stainless steel are used.

Production

Materials of Construction.—Copper, steel, and cast iron have been used for decades in contact with liquid sugars. The serviceability of those metals is evidenced by the fact that there are now in operation many vacuum pans, liquor tanks, and bone-char filters with ages ranging from 50 to 80 years. In recent years many changes have been made in processing sugars; new products have been developed, and changes in construction, as well as new types, of equipment have created new problems in metals. Each refinery has its own variations of processing and its own theories on metals. The result is that several metals indicate good service but have not been in service long enough or in sufficiently wide variety of operating conditions to warrant full approval.

Tin, zinc, copper, stainless steel, aluminum, and Monel are satisfactory in contact with liquid sugars. As far as is known, any metal can be used except lead, which is barred both voluntarily and legally. The questioning of many experienced refiners reveals no instance of the purity of the sugar being affected by metals. Considering the frequent routine tests made by government agencies and large food corporations, the evidence is quite convincing.

Very little research has been done on sugar corrosion, and the behavior of alloys is so unpredictable that values can be determined only by test. The addition or change of a small amount of alloying metal may mean success or failure. In one special process, where corrosion was above normal, all forms of copper, including Monel, were unsatisfactory except one alloy with a copper content of 96 per cent. This same alloy failed when used in another process where the corrosion was less than normal. In one process an aluminum alloy was used and immediately turned black; another alloy of the same metal was satisfactory. Both alloys had an aluminum content of 98 per cent and the same three alloying elements. The difference in the result was caused by changing the relative proportion of the three minor elements by less than 1 per cent.



Key. Carb., carbonators; Sulph., sulphitors; F., filters; W, wash water, C, centrifugals; Con., condensers; D, dissolvers

Note: About half of all plants use sweet water from filter washing for slaking lime, others use fresh water

Beet sugar.

1. Steel with firebrick lining
2. Rotary steel burner with cast-iron combustion chamber
3. Steel
4. Steel, calorizators are steel equipped with copper tubes
5. Steel
6. Steel
7. Steel
8. Cast iron
9. Steel or cast-iron shell with redwood or cypress baffles
10. Cast iron
11. Steel or cast-iron shell with redwood or cypress baffles
12. Cast iron
13. Steel shell, copper-bearing steel tube sheets, tubes are hard-drawn copper annealed full length or admiralty bronze
14. Steel curbs and baskets, Monel stabbed linings, bronze backing-up screens
15. Steel
16. Steel with revolving screen of brass in discharge end
17. Copper-bearing steel shell with copper steam coils
18. Steel
19. Steel curbs and baskets, Monel stabbed linings, bronze backing-up screens
20. Steel
21. Copper-bearing steel shell, tube sheets, and tubes
22. Copper-bearing steel shell, tube sheets, and tubes
23. Steel
24. Steel curbs and baskets, Monel stabbed linings, bronze backing-up screens

Scaling, confined generally to steel and cast iron, causes minute black specks in the sugar which, though not harmful in any way, might be revolting to a customer if he should find one in a piece of clear candy. Specks cannot be eliminated, so they are a constant irritation to the refiner, who does his utmost to keep them at a minimum.

The above discussion has been of metals completely submerged in cane sugar solutions. A more corrosive action occurs when vapors are present in an enclosed vessel. The modern trend is to enclose such equipment as liquor tanks and blowups, which from time immemorial have been emitting vapors causing a mild corrosion of structural steel and destroying paint. Refineries have tried many alloys, but there is little agreement in results, and all are seeking better materials.

Vapors arising from bone-char processes are strongly corrosive. Those coming from the kilns and dryers are not corrosive if their temperatures are maintained above the dew point. Cast-iron retorts in kilns have been superseded by thin-walled retorts of 16 to 18 per cent chrome steel. The only corrosion of these retorts comes from fuel combustion gases and is not too harmful if the carbon content of the metal is below 0.1 per cent. Char waste water contains some sulphur, but practically all of that element flashes off in the open gutters in the liquor gallery.

There are many cast-iron and steel bodies in the industry that have been in service for many years and have corroded to the point where they will have to be replaced in a few years if further corrosion is not prevented. This state of affairs offers quite a field for protective coatings, and many tests are being made. Care must be taken to avoid coatings that contain elements which should not be used in contact with food. Some experimental programs have been prolonged because specimen tests were misleading. In some isolated cases, more expensive coatings have lasted longer but not sufficiently to warrant the additional expense. Some expensive coatings will give a life of 8 to 10 years and with some patching will probably last 5 or 6 years longer. At the present time there is not sufficient field experience to indicate the most satisfactory type.

The clarification of sugar sirup frequently involves the use of char, which has to be filtered out of suspension with or without the use of filter aid material. Worthite pumps have been used successfully over a 7-year period for this service. Sugar evaporators or pans have been unloaded by centrifugal pumps made of the same alloy.

Raw-cane-sugar Process.—Equipment and processing used in one of the newest sugar mills in the country, the Iberia Sugar Cooperative at New Iberia, La., has been described. (Pace, G. L., Making Cane Sugar for Refining, *Chem. & Met. Eng.*, Vol. 48, No. 7, pp. 77–79, 1941.)

Sugar cane is delivered at this mill in trucks, railroad cars, and barges and transferred either directly to the steel tables or to storage in the yard by derricks. These steel tables feed cane onto the carriers. Attached to the carriers is a set of knives mounted on self-aligning bearings in a heavy steel-plate housing. These knives chop the cane into chips. These chips are passed through the steel crushers, which disintegrate the cane and express about 75 per cent of the juice. The crusher is followed by a series of four three-roller mills, which continue the extraction of the juice until about 94 per cent of the sucrose in the cane has been removed.

The raw juice flows from several compartments of the trough beneath the mills to strainers, where small pieces of bagasse are removed. Stainless-steel pumps convey the screened juice to a scale. These pumps have stainless-steel bodies, runners, and shafts.

After treating the juice with lime, it is heated to 220°F. before passing to settlers. The heaters have welded-steel bodies. The tubes are of copper rolled into steel tube sheets.

The hot juice limed to the suitable pH is pumped by a steel pump into the continuous clarifier and allowed to settle. Clear juice passes to the steel evaporator supply tank, and the muds are pumped by a steel pump to the filter station, where they are fed to a continuous vacuum filter. The juice is recovered from the muds.

The clear juices are pumped by steel pumps to a quadruple-effect evaporator. The bodies are cast iron; tube sheets and tubes are copper. The sirup is then pumped to vacuum pans. The bodies of the pans are of welded Toncan iron construction with the tube sheets and downtakes made of the same metal. Toncan iron tubes are rolled into the tube sheets. The vacuum pans concentrate the evaporator sirups to 90 to 95°Brix, and this semiliquid is known as "massecuite."

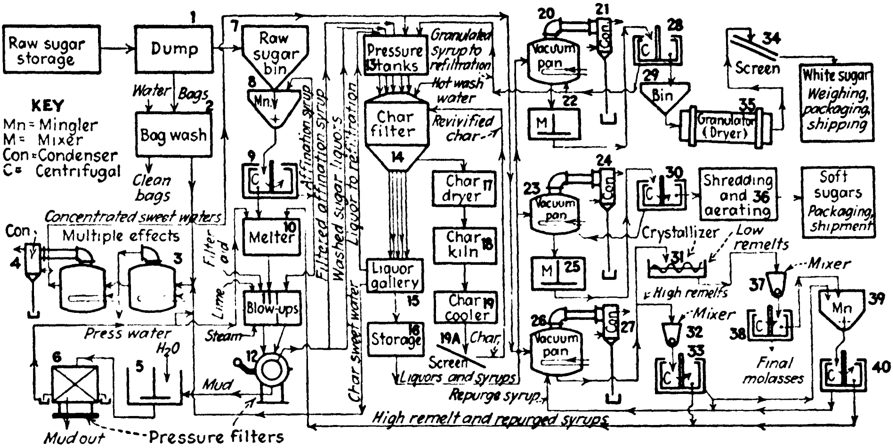
Crystallizers process the massecuite before purging in the centrifugals. Here the strikes of the first sugar pan are stored until ready to be sent to the centrifugal mixer. The sugar resulting from the first strike runs between 96 to 97 per cent sucrose and passes directly to the bagging station. This is commonly known as "raw sugar" and is shipped to refineries for further processing.

Sirup thrown off the sugar by centrifugal force contains 35 per cent sucrose. It passes to the steel pan supply tanks where it is used with evaporator sirup to make up first strikes for the vacuum pans. The sugar resulting from a second sugar machine contains about 26 per cent sucrose.

The sugar resulting from a third sugar strike is mingled with sirup or high-grade molasses to be used for seeding the vacuum pans. The runoff is the final molasses and is sold as commercial molasses.

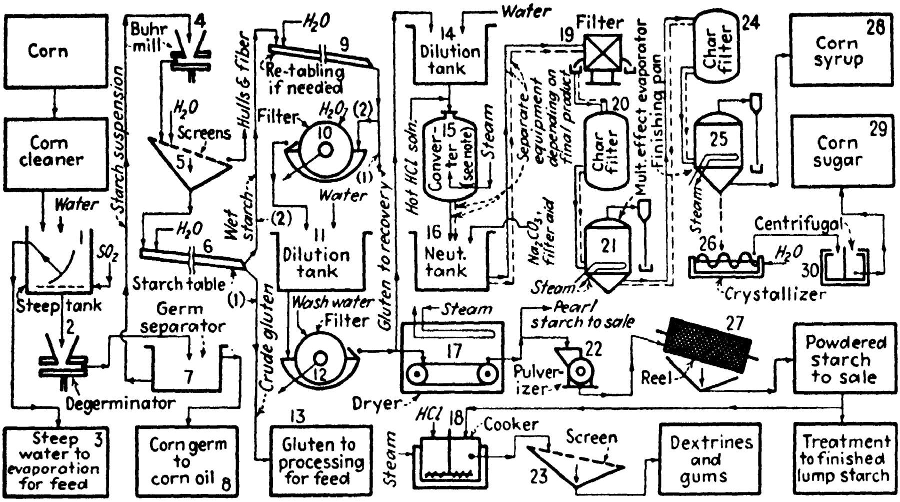
Refining Process.—In one refinery raw sugar is fed to minglers and affination centrifugals. The washed sugar is dissolved in the melter at low temperature and high Brix. The solution is treated with calcium phosphate as coagulant, hydrated lime as precipitant, and a sterilizing agent and decolorizer. A proper combination of these reagents precipitates most of the colloidal organic impurities and coloring matter, which are flocculated by the application of heat in a continuous flotation clarifier. All the added reagents are eliminated with the impurities. Floc is flotated to the surface, and clarified liquor is ready for final decolorization.

Clarified liquor is treated with decolorizer, filter aid, and dechlorinator and pumped through a battery of rotary pressure filters. The resulting filtrate is a sparkling white liquor of exceptional clarity and purity. It is concentrated to 70°Brix in the triple-effect evaporator and sent to the vacuum pan for crystallization.



Refined cane sugar.

1. Cast-iron body, steel shaft, cast-steel breakers
2. Cast iron, steel
3. Cast-iron body, copper tubes and sheets
4. Cast iron
5. Steel
6. Cast-iron body and plates, brass screens
7. Wood lining
8. Steel
9. Steel casings, steel or bronze basket, steel spindle
10. Steel
11. Steel
12. Cast body, bronze leaves and screens
13. Steel
14. Cast iron
15. Copper and cast iron
16. Steel
17. Cast iron
18. Iron castings with chrome-steel tubes
19. Iron castings with sheet-iron tubes
19*a*. Steel
20. Copper
21. Cast iron
22. Steel
23. Copper
24. Cast iron
25. Steel
26. Copper
27. Cast iron
28. Steel casings, steel or bronze baskets, bronze screen, steel spindle
29. Wood
30. Steel casings, steel or bronze baskets, bronze screen, steel spindle
31. Steel
32. Steel
33. Steel casings, steel or bronze baskets, bronze screen, steel spindle
34. Steel frame, bronze screen
35. Steel
36. Steel, brass
37. Steel
38. Steel
39. Steel
40. Steel casings, steel or bronze baskets, bronze screen, steel spindle



Note: Degree of hydrolysis controllable by time, temperature and concentration in converter, thus permitting different end products, such as sugars or syrups

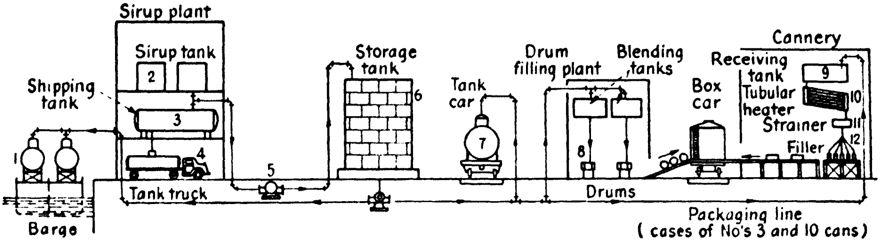
Corn sugar and other corn products.

1. Wooden cylinder with cast-iron cone at bottom
2. Steel plates with cast-iron housing
3. Steep water evaporator: body, cast iron; tube sheet, Type 316 stainless steel
4. Buhr mill: grinding surfaces, buhrstone or carborundum; housing, stainless steel
5. Nylon bolting cloth on wooden framework or Type 316 stainless steel screens
6. Wood
7. Wood
8. Ordinary steel or cast iron
9. Wood
10. Tanks: Type 316 stainless-steel cladding; spokes, Type 316 stainless steel or Everdur; decks, wood with nylon filter cloth
11. Type 316 stainless steel or wood
12. Tanks: Type 316 stainless-steel cladding; spokes, Type 316 stainless steel or Everdur; decks, wood with nylon filter cloth
13. Ordinary steel or cast iron
14. Type 316 stainless steel or wood
15. Bronze
16. Wood
17. Perforated stainless-steel belt, framework and housing, ordinary steel
18. Steel
19. Sweetland filter: filter leaves, Type 316 stainless steel; filter cloths, cotton duck; shell, cast iron
20. Cast iron
21. Body, cast iron; tube sheet, copper or Type 304 stainless steel
22. Steel with bronze hammers
23. Stainless-steel screens
24. Cast iron
25. Body, cast iron; tube sheet, copper or Type 304 stainless steel
26. Stainless-steel-clad interior, rest ordinary steel
27. Stainless-steel screen
28. Steel with copper cooling coils
29. Stainless steel
30. Baskets, stainless steel or bronze; screens, stainless steel, bronze, or Monel

The standard vacuum-pan system of crystallization produces in conjunction with centrifugals several strikes of wet white sugar. These strikes are mixed together and passed over successive heating and cooling drums of a rotary horizontal granulator. The sugar is sifted through magnetic vibrating sifters, in which it is classified according to grain size. The finished dry sugars are packed and sent to the warehouse.

Packaging

Sugar is shipped in wooden barrels and cloth or paper bags.



Liquid sugar.

1. Phenolic-resin-lined
2. Stainless steel
3. Stainless steel
4. Stainless steel
5. Stainless steel
6. Steel painted with aluminum on outside and lead-free tropolite on inside
7. Phenolic-resin-lined
8. Phenolic-resin-lined
9. Stainless steel
10. Stainless steel
11. Stainless steel
12. Stainless steel

SULPHATED OILS

The sulphated oils, long used as wetting agents and penetrants, are made from a variety of animal and vegetable oils including castor, olive, tea seed, corn, peanut, lard, neat's foot, and fish oils. They sometimes are referred to as sulphonated oils but more correctly are sulphated oils, since the bond is mostly through the oxygen of a sulphate group. A common representative of this class of materials is sulphated castor oil, known as Turkey red oil, used in textile dyeing. (International Nickel Co., *Tech. Bull.* T-3.)

Production

Materials of Construction.—Test results are indicative of the good performance of Monel in the sulphation of animal and vegetable oils, which has been confirmed by its performance in operating reactors over a period of years. Monel is used for the construction of complete sulphators, linings, heating coils, agitators, pipe, fittings, pumps, and pump rods. Corrosion resistance is favored by the fact that the concentrated acid when added is dispersed in the oily medium, which provides a somewhat protective film. The ultimate use of most sulphated oils calls for a product of high purity with minimum discoloration. Users have observed that in most cases oils processed in Monel equipment are equivalent in color to those processed in glass. In the case of sulphated olive and tea-seed oils, there is some indication that nickel sulphating equipment may give better color. Monel also has good resistance to corrosion by the diluted sulphuric acid and the alkalis encountered in washing and neutralization equipment. The nickel-chromium-molybdenum-iron alloys are used for pumps and valves in sulphation and washing systems, since they have suitable resistance to both concentrated and dilute sulphuric acid at the temperatures encountered. Type 1 Ni-Resist can be used to some extent for pumps and valves, although its corrosion rate usually is higher than the other materials mentioned. (*Ibid.*)

Glass-lined reactors are satisfactory for these sulphonations, irrespective of temperature or H_2SO_4 concentration.

Lead-lined vessels are in common use for the treatment of animal and vegetable oils with concentrated sulphuric acid in the manufacture of sulphated oils.

Sulphating tanks, heating coils, and pipe of Type 316 stainless steel have proved satisfactory where there is no dilution of the 66°Bé. acid.

Chlorimet 3 is giving excellent results in fatty-acid sulphonation with dilute sulphuric acid. Temperature reached is 175°F.

Sulphonators are sometimes fabricated of cast iron of suitable composition. Frequently corrosion of such equipment is accelerated by the presence of air, generally at the liquor level, on account of both its oxidizing effect and its moisture content, which may locally reduce the concentration of the acid.

Process.—Sulphating of animal and vegetable oils usually is done with 66°Bé. sulphuric acid at temperatures from 68 to 140°F., and with good agitation during reaction. With some of the more highly unsaturated fats, temperatures must be kept in the neighborhood of 50°F. Sulphating usually is done in batches which may require from 6 to 24 hr. depending upon the size of batch and the nature of the oil. After sulphating, sodium sulphate or sodium chloride solutions are added to salt out the product, which is separated, washed with glauber's salt solution, reseparated, and finally neutralized with caustic soda, soda ash, or ammonia. Frequently, washing and neutralization are done in the sulphation vessel. (International Nickel Co., *Tech. Bull.* T-3.)

Handling

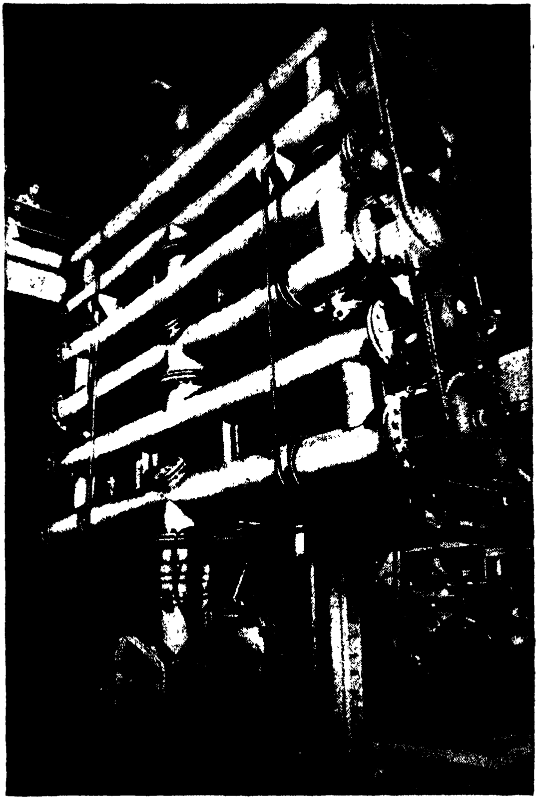
Nickel-clad and Inconel-clad steels are used for the storage of finished sulphated oils. The use of the clad steels for large tanks provides economy as well as protection for the product.

SULPHATE PAPER

Sulphate pulp that has been produced in the pulp mill must have certain coating, coloring, sizing, and other chemicals added to it and must be refined before it can be made into paper or board.

Production

Materials of Construction.—Some idea of the quantities of various materials that are used in the construction of a Fourdrinier paper machine may be had from information recently published. (Anon., Pulp and Paperboard Plants of Southern Paperboard Corp. Start Manufacturing, *Southern Pulp Paper Mfg.*, pp. 26–28, Aug. 15, 1948.) A 236-in. kraft liner-board machine required 1,340 tons of iron castings, 6½ tons of brass castings, 156 tons of steel castings, 20 tons of steel forgings, 115 tons of steel plate, 33½ tons of mild steel, ½ ton of stainless steel, 1,165 lb. of brass plate, 850 lb. of copper, 2 tons of aluminum, 3 miles of steel pipe, 492 ft. of steel rod, 6½ tons of Monel, 160 lb. of Everdur, and 1,330 lb. of Micarta.



Reaction chambers of Chemi-pulpers fabricated of 20 per cent stainless-clad steel.

The Fourdrinier machine is equipped with a bronze shell breast roll, Micarta bladed forming board, rubber-covered table rolls, Monel suction boxes, Monel-covered return wire rolls, stainless-steel save-all pans, and rubber-covered suction press rolls with rubber-covered upper rolls. The felt rolls are all rubber-covered. There is a Monel-covered receiving roll. A Transite hood is over the dryer section of the machine.

Process.—The pulp from the mill is pumped to a concrete mixing chest where rosin size and certain other materials can be added. After mixing, the stock goes to a beater chest where other materials are added. It is then refined. Refining consists of a hydrating treatment in steel refiners. The stock discharges into concrete storage chests from which it is pumped through finishing refiners. It may then go into a machine chest, where alum is added. The stock is then ready for the Fourdrinier machine, so it is pumped to the head box which may be wood or steel. Some mills use neoprene-lined steel head boxes. Others use stainless-steel boxes. From the head box the stock goes onto the wire of the machine and then through the rolls and comes out the dry end of the machines as dry paper, which is then calendered and trimmed to desired widths.

SULPHATE PULP

Almost every pulp mill built in recent years has been designed and equipped to use the sulphate (kraft) process. Although the alkaline liquors that are handled are not generally considered to be so corrosive and otherwise troublesome as those encountered in the acid sulphite process, there are numerous extremely severe conditions such as the evaporation of black liquor.

Production

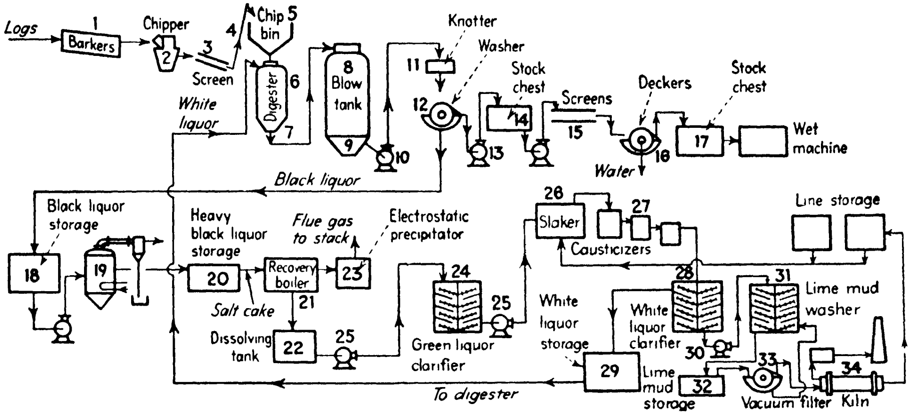
Materials of Construction.—While in former years almost all equipment in the sulphate pulp mill was made of plain iron and steel, wood, concrete, and tile, more recently considerable stainless steel and other new materials of construction have been installed.

Process.—The basic procedures in sulphate pulping are as follows: Caustic soda and sodium sulphide are mixed with wood chips in a digester and cooked. The mixture is then blown into tanks known as "diffusers" or over vacuum washers. The spent cooking chemicals are removed. The stock passes onto a screen, then to a thickener, and finally into a stuff chest. From this chest the stock passes to a screen where much of the water drains off and then into a bleaching unit. After bleaching, it goes to the final operation, which is a pulp press.

The principal raw material, wood, is stored in the wood yard. From here it is carried by steel conveyors to the copper-bearing steel barking drums, where the bark is removed. After sorting and inspection on another steel conveyor, the clean wood goes to chippers. Alloy chipper knives in many cases are showing superiority over carbon-steel knives. The chips go by rubber belt or steel conveyor to a perforated steel or wire chip screen. Chips of the correct size pass through the screen and are carried by a rubber belt conveyor to storage bins. These may be tile or concrete silos or wood or steel bins. Feeders below the opening in these bins or silos deliver chips onto a rubber belt for distribution into any one of the digesters.

The cooking of the chips is done in digesters with cooking liquor, known as white liquor, and steam. The digesters are usually made of mild steel, firebox steel, or boiler plate. Both Inconel-clad steel and Type 347 stainless-clad-steel digesters are in use.

Some mills prefer to line the digesters with carbon brick. The brick that is now being used runs 50 to 100 per cent higher in strength than regular carbon brick and at the same time has a coefficient of expansion approaching that of the digester sheet. This will reduce over-all lining thickness from 5 to 3 in.



Sulphate (kraft) pulp.

1. Copper-bearing steel
2. Alloy steel, plain or carbon steel
3. Steel
4. Rubber
5. Concrete, wood, steel
6. Carbon steel, firebox steel, boiler plate, carbon-brick lining
7. Stainless steel, Monel
8. Carbon steel, ingot iron
9. Type 304 stainless steel
10. Type 304 stainless steel
11. Carbon steel, stainless steel
12. Carbon steel, Type 304 stainless steel
13. Carbon steel, stainless steel
14. Concrete
15. Chrome or nickel-plated, stainless steel
16. Bronze, stainless steel
17. Tile-lined concrete or steel
18. Steel
19. First, second, and third effect tubes, Type 304 stainless steel or carbon steel; third and fourth effect tubes, plain steel
20. Steel
21. Brick-lined
22. Steel with cast-iron agitator
23. Steel
24. Steel
25. Stainless steel
26. Steel tank and stainless-steel mechanism
27. Brick or concrete-lined steel tank and stainless-steel mechanism
28. Steel
29. Steel
30. Stainless steel
31. Steel
32. Steel
33. Cast-iron drum and stainless-steel or Monel screen
34. Brick-lined steel shell

Carbon bricks are used principally in two locations: (1) in old riveted digesters which have lived their normal life as unlined digesters, in conventional cooking practice, and (2) in new or comparatively new welded digesters where increases in pressure, temperature, and corrosive conditions over what was conventional a few years ago are now practiced.

"The first case is obviously principally a matter of deciding whether or not it is cheaper to buy a new welded digester and cook on the bare metal or to line a riveted job and extend its life an, as yet, undetermined number of years. In one case 15 years were obtained from a lining.

The second case occurs principally in Southern mills which started off with new welded shells. Such shells had shown practically no corrosion in Northern mills but in some of the Southern plants were called unsafe after 8 or 10 years. The cooking conditions differ. Some of these Southern mills, it is said, cook with sodium sulphite as well as the regular sulphate liquor, which, of course, complicates the corrosion problem on base metal.

Because of combined erosion and corrosion in the case of plain steel in the conical portion of the digester some mills have either stainless-steel or Monel sheets welded into the lower parts of cones.

Both Types 308 and 317 stainless steels are used with success for digester circulating pumps. Among the other metals in use for this purpose are a 29-9 chrome-nickel steel and Ni-Resist. Some mills use a casing of nickel cast iron and impeller, nut, and sleeve of stainless steel. In another case the body is semicast steel (4 to 5 per cent nickel) with Type 317 stainless-steel impeller, shaft, and seal ring.

For steam and liquor inlets and outlets on digesters most mills use ordinary iron and steel. Many mills use 18-8 or other stainless steels for nipples and nozzle linings. Type 317 stainless-steel-trimmed valves have proved satisfactory. Monel also is used to some extent for this purpose. Both of these metals and Ni-Resist are used for blow valves. For digester sleeves 18-8 stainless steel, extra-heavy steel, and Monel are all reported as being satisfactory.

Tubes for indirect heaters for the digesters are made of any one of several metals. Type 316 stainless steel is generally favored, but plain steel, Inconel, and Monel are also used. Stainless steel has prevented trouble in the surface condensers used for condensing the blowoff steam from digesters.

When the cooking operation is completed, the spent cooking liquor is separated from the usable cellulose fibers either in diffusers or in washers. The trend at present is away from the use of diffusers.

The diffusers are fabricated of plain steel, 18-8 stainless steel, or Monel. The bottoms are ordinary steel. Screens are Monel or stainless steel.

It is now customary at the end of the cook for the complete charge from the digester to be blown out by its own pressure and into the blow tank. These tanks are made of ordinary steel or ingot iron, but the conical bottoms and perforated plates of these units are 18-8 stainless steel to prevent erosion and corrosion.

Pulp and liquor from the blow tank are screened in a knotter of plain or stainless-steel construction throughout to remove knots. The pulp and liquor are then passed over a rotary washer system equipped with mild-steel, Monel, or 18-8 stainless-steel screens to separate spent cooking liquor from pulp. Structural parts of the filter are made from alloy cast irons containing up to 50 per cent nickel. The black liquor drops from each washer in the system through a vacuum leg to a tank in the recovery plant.

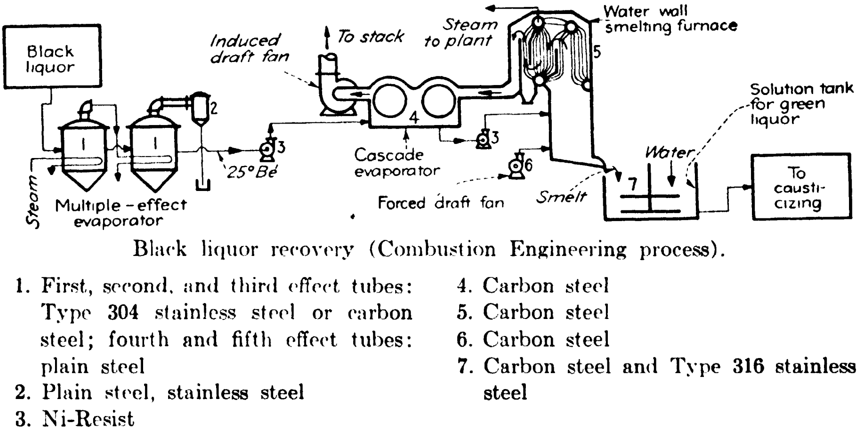
The washed stock is discharged by gravity from the washers into concrete storage chests equipped with agitators. From storage it is pumped by a plain steel pump to a mixing box, where white water is combined with it. The stock is next passed over rifflers and screens. In the case of plates for flat screens, bronze castings are used. It is customary to chrome-plate these plates, although some mills have also used nickel plating. The latter is preferable to the chrome when hydrochloric acid is used to clean the plates, nickel having greater resistance than chromium to the acid. A newer development in flat screens is the use of thin stainless-steel sheet reinforced.

Accepted stock from the screens flows by gravity through a decker, where it is thickened. The screens of the deckers are made of bronze or stainless steel.

White water from the thickeners discharges through a drop leg into a concrete storage tank under the washed stock chest from which it is recirculated.

Thickened stock goes to stock chests. These are frequently tile-lined concrete or steel. After the consistency of the stock is regulated, it may go to a wet press, where it is made into wet lap for shipment, or to the paper mill for bleaching, refining, and making into paper on the Fourdrinier machine.

Chemical Recovery.—In the recovery of chemicals from the spent cooking liquor are found some of the most troublesome corrosion problems. Black liquor recovered from the stock-washing operations is stored in large tanks or chests. From these it is pumped to multieffect evaporators in which it is concentrated from 15 or 16 to 50 to 55 per cent solids. For the first-, second-, and sometimes fifth-effect tubes of the evaporators Type 304 stainless steel has been found satisfactory. A few mills have chrome-plated the steam side of the fifth-effect tubes. Plain steel is satisfactory for the other effects. Some mills also use plain steel for all effect tubes with fair success. In some mills 3, 5, and 9 per cent nickel-steel tubing are used. In many of the newer installations the tube sheets, lower body, and top deflector of effects 1 and 2 are stainless clad. The pumps



Black liquor recovery (Combustion Engineering process).

1. First, second, and third effect tubes: Type 304 stainless steel or carbon steel; fourth and fifth effect tubes: plain steel
2. Plain steel, stainless steel
3. Ni-Resist
4. Carbon steel
5. Carbon steel
6. Carbon steel
7. Carbon steel and Type 316 stainless steel

used to transfer the liquor between stages are Worthite or other stainless steel in some of the new mills. Others use ordinary carbon steel.

The concentrated liquor goes to storage tanks. It is next pumped to a cascade-type evaporator and finally to recovery boilers.

Hot waste gases from the recovery boilers after passing through the cascade evaporators go to an electrical precipitator for the recovery of salt cake. This salt cake is conveyed to a mixing tank, where it is mixed with weak wash water from the causticizing plant or black liquor and then returned to the disk evaporator.

Make-up salt cake is handled pneumatically to mixing tanks, where it is combined with black liquor feeding into the recovery unit. The smelt from the recovery unit is mixed with weak liquor from the recausticizing operation to form green liquor, which is pumped to storage tanks. The green liquor before being used in the causticizing operation is clarified in trays, and the dregs resulting are washed for recovery of soda in tray thickeners.

Clarified white liquor is added to reburnt lime in a slaker with a classifier for removing dirt. Unlined steel tanks are used for slaking lime in many mills. Others prefer tile, brick, or concrete linings. The most recent installations consist of steel tanks and stainless-steel mechanisms.

Resulting milk of lime is pumped to causticizing tanks. Causticizers in the newest plants are steel tanks with brick or concrete lining and stainless-steel mechanism. The causticizers discharge by gravity to the tray clarifier and mud-washer trays. The clarified white liquor goes to storage tanks until required for the digesters. The vacuum filters used in the causticizing operations and the centrifugal pumps are stainless steel.

A wide variety of materials of construction is used for pumps handling the many liquors and sludges throughout the pulp mill. Monel is used for pump shafts and impellers in pumps handling black, green, or white liquor under all conditions and for removing condensate from evaporator steam chests. Hardened Monel has been found satisfactory for pump shafts and rods where abrasion, as well as corrosion, is a problem. White liquor is handled by 18-8 stainless steel throughout or by cast-steel bodies with 18-8 stainless shaft sleeves, impellers, and shrouds.

Cast iron is used for pumps handling milk of lime. Other materials that have been used successfully are chilled iron, 3 and 5 per cent nickel iron, 18-8 stainless steel, Ni-Resist, and low-chromium–low-nickel cast iron.

Pumps for handling liquids containing abrasives in suspension can be cast iron. Other plants prefer cast-iron shells and impellers with shafts made of Monel. Worthite, manganese steel, high-silicon iron, and 3 per cent nickel cast iron are also used. Yet others specify cast steel, plain steel, or stainless steel. All stock pumps can be of cast iron.

Piston-type pumps handling black stock (with liquor) can be of cast iron except the plunger, which should be stainless-steel-clad metal or cast iron with a stainless-steel sprayed coating. Alum solutions containing free sulphuric acid can be handled by high-silicon iron pumps.

It is customary to use plain cast-iron or alloy cast-iron valve bodies on black, green, or white liquor. These valves are generally trimmed with Type 304 or 317 stainless steel or Monel. Where the black-liquor conditions are more severe, *e.g.*, on evaporators, Ni-Resist is used with success.

Sulphate mills are using a wide variety of piping materials for handling cooking liquors, milk of lime, and other solutions. Plain iron is generally used for milk of lime, while low-chromium–nickel steels are favored by most engineers for cooking liquor, green liquor, and black liquor. Ni-Resist pipe has been used for handling condensate from black-liquor evaporators. Wrought iron is in use for handling liquors. Some mills continue to use plain steel and cast iron for these solutions.

SULPHATE PULP, BLEACHED

Production

Materials of Construction.—The Materials of Construction Committee of the Technical Association of the Pulp and Paper Industry has made a survey of the experience of the mills that were bleaching sulphate pulp.

Experience differs with chlorinating vessels made of concrete and lined with tile plates. In one case tiles have not required frequent replacement nor has pointing up been necessary. The reverse was true in another mill, where silicate and portland cement were employed for pointing up. An unlined concrete vessel proved satisfactory. No crumbling of the concrete at the surface was noticed. A hollow-tile vessel was satisfactory in another mill. A vessel of 18-8 stainless steel containing molybdenum has lasted 2 years and is still good. A steel vessel protected by chlorinated rubber-base paint is in use. After 1½ years it became necessary to repaint above the water line. In one mill a steel vessel lined with hard rubber has required no repairs in 5 years.

From a corrosion point of view if the vessel is to be used only for chlorination or for chlorination and neutralization, it is recommended that it be made of tile-lined concrete, rubber-covered steel, wood, or steel protected by chlorinated rubber-base paint with rubber covering above the water line.

Rubber-covered steel is recommended by three mills for impellers in chlorinators. Other mills prefer straight 18-8 stainless steel and steel containing molybdenum. Durimet is said by another report to be very satisfactory after 2 years.

Where chlorine gas is fed directly to the chlorinator, rubber-covered steel and Hastelloy C have proved most resistant to corrosion when used as a diffuser.

Various materials are recommended for lead-in pipe for chlorinator: Pyrex glass, glass-lined steel, lead, rubber-covered steel, and others. Plain iron was reported to have a life of 12 to 18 months. Rubber-covered steel has lasted 6 to 7 years. Plain iron pipe has been found to be satisfactory for dry chlorine gas, but if moisture is present, rubber hose must be used.

Where chlorine is fed in water solution to the chlorinator, rubber-covered steel has proved most resistant and longest lived for carrying the water-chlorine mixture. It has had a life of 6 to 7 years.

Hastelloy C, high-silicon iron, and 18-8 stainless steel containing molybdenum (must be annealed after mechanically working) are recommended as the best materials for the ejector.

The materials that have proved most satisfactory for dump valves of chlorinators where the stock is dumped acid are rubber-covered steel, stainless steel, and Durimet. Where the stock is dumped neutral, 18-8 stainless steel or Durimet should be used.

The materials that have proved most satisfactory for stock pipes when dumped neutral are steel and wood-lined steel. A transfer line made of wood-lined steel is still satisfactory after 2 years' service.

The material best suited for stock pumps where the stock is pumped acid is reported to be high-silicon iron; where it is pumped neutral, cast iron and 18-8 stainless steel containing molybdenum.

Monel metal and 18-8 stainless steel containing molybdenum are reported satisfactory for washers when stock is washed acid. Where the stock is washed alkaline or neutral, Monel wire is reported as lasting 12 to 18 months, bronze as lasting 6 months, stainless steel is still good after 2 years.

In the process of caustic extraction the materials that are reported best for the extractor are reinforced concrete with tile lining, cast iron, and stainless steel.

In the hypochlorite bleaching stage the material reported to be best suited for bleachers is tile-lined concrete which has lasted 1½ years in one mill and is still good. In another it was repainted in one spot after 15 months. Another reports that concrete lasts indefinitely. Two other mills report using concrete-filled tile. In one it is said to have had an indefinite life.

Materials that are said to be best for impellers for high density are bronze, cast iron, and nickel iron. In the case of low density, the materials recommended for impellers are Promal, Z metal, and cast iron.

The types of washer-covering best suited for washing pulp after the hypochlorite stage are reported as being Monel by three mills (in a fourth mill this metal has not been satisfactory), bronze, and 18-8 stainless steel containing molybdenum.

The one mill reporting use of a bleach treatment after the final hypochlorite bleach uses tile and Asplit. The SO_2 is said to be pH controlled. This reagent has a very corrosive effect on linings for the vessel. The flash treatment is not given in the same vessel as the final hypochlorite bleach.

The materials reported as best suited for valves, pipe lines, and stock pumps for stock after final hypochlorite treatment are wood, stone and rubber-lined fittings, cast-iron pump and steel pipe, cast iron, bronze, high-silicon iron, CNI (chrome-nickel, iron) valves, copper pipe line, and stock lines of cast iron with a bronze impeller.

Materials reported as giving best results for bleach liquor make-up and storage tanks are concrete, steel painted with chlorinated rubber-base paint, and hollow tile. The materials for pipe lines are high-silicon iron, rubber hose, cast iron, and CNI. One mill has had plain iron last 2 years. Cast-iron and bronze pumps handling bleach liquor have lasted from 2 to 3 years in two mills. In another mill 18-8 stainless steel containing molybdenum has given satisfaction.

Materials reported best for handling fumes from bleachers, chlorinators, etc., are as follows: (1) for piping, one mill prefers steel and two like Transite; (2) for ducts, two specify Transite and one reports Transite and Masonite; (3) for fans, ordinary steel, rubber-covered steel, chlorinated rubber-painted steel, and steel coated before assembly with baked Heresite paint have given satisfaction. This paint resists saturated chlorine fumes for 1 year or longer. Bolts should be 18-8 stainless steel containing molybdenum. All joints of metal not welded before coating should have a Heresite layer between joints.

The steel framework in the bleach building is protected by several types of paints. Iron oxide primer is still good after 1 year. Aluminum paint is used satisfactorily. White lead is used in another mill, but it is stated that chlorinated rubber-base paint is used on all framework and equipment with complete satisfaction.

It is the practice in one mill not to cover the chlorinator and bleachers. In two others bleachers have concrete covers. Wood and Transite covers are reported used in mills.

Both plug and diaphragm types of valve have been found to be effective and long-lived for handling bleach liquor. The metals recommended are high-silicon iron and 3 per cent nickel cast iron or CXI body trim of 18-8 stainless steel containing molybdenum.

Three mills report that in making bleach liquor chlorine is absorbed through a lateral with pump circulation. Ordinary steel laterals with 18-8 stainless steel containing a molybdenum chlorine inlet tube are reported satisfactory. High-silicon iron and Hastelloy C are also reported in use. The latter is reported to have lasted 4 or 5 years. In one mill a concrete box equipped with a cast-iron agitator is said to have an indefinite life. Another mill uses an open tank with perforated lead pipe on the bottom.

The special treatments that have been effective in combating corrosion in and around the bleach plant are Heresite, chlorinated rubber-base paint, asphalt paint, and lead covering. The rubber-base paint is strongly favored by almost every engineer who has anything to do with a bleach paint.

Bleaching.—Sulphate pulp can be bleached by a batch or continuous process. Chlorine and hypochlorite solutions are used for the bleaching. To handle these solutions and the caustic that is also used such materials of construction are used as rubber, tile, stainless steel, concrete, and wood.

Process.—The process and materials of construction used in the new continuous multistage process of the Nekoosa-Edwards Paper Co.'s plant at Nekoosa, Wis., were described by Nugent. (Nugent, R. A., New Multi-Stage Plant Bleaches Kraft Pulp, *Valve World*, Vol. 45, No. 2, pp. 34–38, 1948.) The unbleached pulp is screened over stainless-steel screen plates and supplied to a tile-lined brown-stock storage chest. From the bottom the stock is pumped through a steel line to a consistency regulator.

The 3½ per cent stock is dropped through a rubber-lined pipe to the basement.

Here chlorine is added, and the stock goes to the first stage of bleaching, or chlorination, which is carried out in a rubber-lined steel chlorination tower. Chlorinated stock flows out of the top of the tower, down through a rubber-lined pipe to the basement, where it is pumped through a rubber-lined pipe to the first-stage washer, which is rubber-covered. Here the pulp is showered with water to remove the noncellulose material made soluble by chlorination.

The second stage in the process is a high-density caustic extraction. From the first-stage washer, stock drops through a stainless-steel chute to a double-shaft mixer, where it is treated with caustic, heated with steam, and then dropped into a tile-lined concrete treatment tower. Treated stock is removed with a screw into a dump chest from which it is pumped through a steel line to a second-stage washer.

The third stage is an oxidation of noncellulose materials with calcium hypochlorite. The stock drops from the washer through a stainless-steel chute to a mixer, where the hypochlorite is added, and then into a tile-lined reaction tower. It is next removed to a dump chest and pumped through a stainless-steel line to a third-stage washer.

The fourth stage is a second caustic extraction carried out in the same manner as in the second stage. Following the fourth-stage wash, pulp stock goes to the fifth and final stage, which is a second oxidation with hypochlorite. After the bleach has been added in a single-shaft mixer, the stock drops through a stainless-steel line to an angle pump suction which forces it into the tower. Bleached stock flows out of the top, drops through a stainless-steel launder line, and is pumped through a stainless-steel line up to the fifth-stage washer, after which it is ready for processing into paper.

The water supply for the plant is brought to the mill through a concrete pipe line. Chlorine, if dry, is handled with Hastelloy-trimmed valves.

SULPHITE PULP

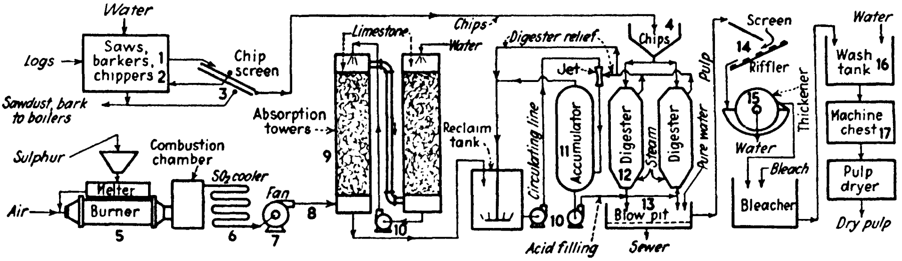
There are generally considered to be more corrosion problems in sulphite pulping than in any other pulp-making process.

Production

Materials of Construction.—Formerly, most equipment was fabricated from lead, copper, or copper alloys. While lead is still the preferred metal for sulphur dioxide gas coolers, much of the other equipment with the main exceptions of acid towers and tanks, digesters, accumulators, and blow pits is stainless steel, Types 308 and 317.

Process.—The process commences with removal of the bark from wood to be pulped. It is removed in a copper-bearing steel drum. Cleaned wood is chipped. Alloy chipper knives in many cases are showing superiority over the plain carbon-steel knives. Chips pass over a perforated steel or wire screen for sizing. Next they are conveyed by rubber belt conveyors to wooden or steel bins or concrete silos. They are charged into a digester, where they are cooked with a mixture of calcium bisulphite and sulphurous acid.

Digesters for regular calcium-base operations are steel lined with silica brick. Type 316 stainless-steel-clad digesters are in service. Type 317 stainless steel is successful for acid lines, relief lines, etc., especially in connection with hot-acid and digester circulating systems. Type 308 stainless steel has given excellent service for collector rings, screens, and similar digester accessories. Valves and fittings which are in contact with cooking liquor are chrome-nickel steels. Relief cooler shells are lead and concrete and cast-iron pipe. All bronze or copper alloys should be eliminated from the cooking system at elevated temperatures to avoid electrolysis.



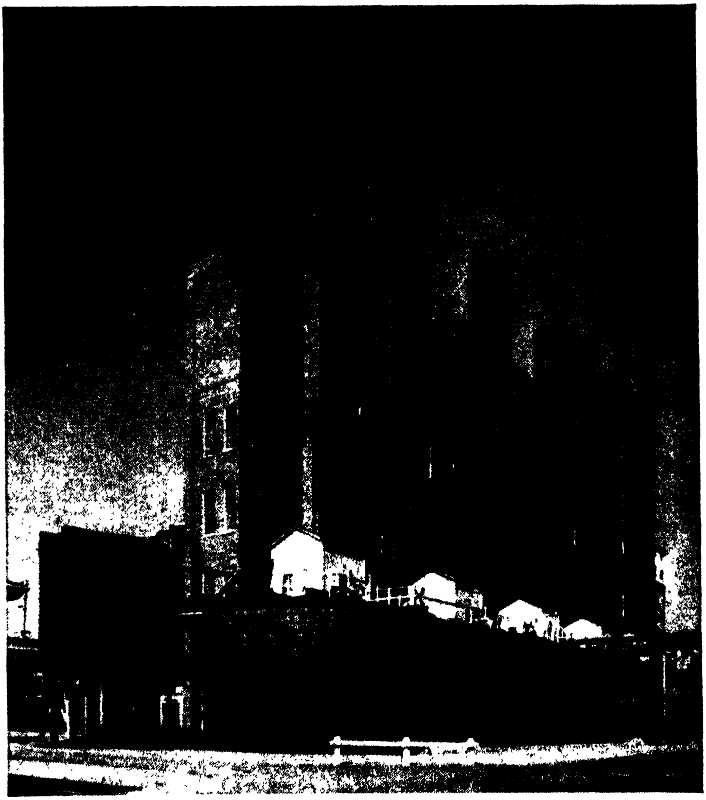
Sulphite pulp.

1. Copper-bearing steel barker
2. Carbon- or alloy-steel knives
3. Steel
4. Wood, steel, concrete
5. Carbon steel and refractory brick
6. Hard lead
7. Hard lead
8. Hard lead
9. Wood, hard lead, or tile-lined concrete
10. Stainless steel, bronze
11. Type 317 stainless steel
12. Steel-lined with silica brick or carbon blocks
13. Bottoms of steel, Type 308 or 317 stainless steel, wood, tile
14. Stainless steel, bronze, chrome-plated plates, copper, Monel
15. Bronze or stainless-steel screen
16. Tile-lined, concrete, steel
17. Tile-lined, concrete, steel

When the cooking of the chips is completed, the contents of the digester are blown to the blow pit. Both cast iron and bronze have been used commonly for blowpipes on sulphite digesters. Ni-Resist also has been used. Probably the most suitable material for blow lines is stainless steel. This is particularly worth while where the pulp is for the rayon industry. The perforated bottoms used in blow pits and drainers are steel, stainless steel, wood, or tile. The use of Type 308 or 317 stainless-steel perforated bottoms and targets has been successful. In fact, stainless steel has proved to be superior to either acidproof tile or wood for bottoms, being nonplugging and less easily dislodged in service. Pulp draining and washing are facilitated.

As for blow-pit accessories, stock valves and save-all plates are 18-8 stainless steel, shower pipes of lead and bronze. Stock lines from pits to stock chests are of Type 317 stainless steel in some cases. Other mills are using wood-lined steel with good results. Blow valves and stems of stainless steel are satisfactory and avoid electrolysis due to dissimilar metals.

Pulp after washing is screened in a knotter of plain or stainless-steel construction throughout to remove knots. The pulp is passed over rifflers and flat or rotary screens. In the case of plates for flat screens bronze-rolled metal is used. It is customary to chrome-plate the plates, although some mills have also used nickel plating. A newer development in flat screens is the use of thin stainless-steel sheet reinforced. Screen plates for the rotary screens may be copper, Monel, or stainless steel, although the last tends to become brittle and crack owing to the cold wash.



Blow pits and vomit stacks in front of digester building, with waste sulphite liquor tank serving the alcohol plant on stilts at left. The digesters run through this building for a height of four stories. Pits and stacks were made of red fir.

Screened stock passes to deckers, where it is thickened. The screens of these machines are made of bronze or stainless steel. Thickened stock goes to stock chests or stuff chests. These are frequently tile-lined, concrete, or stainless steel

After the consistency of the stock is regulated, the stock goes to a wet machine, where it is made into wet lap for shipment.

The cooking liquor is made from sulphur, which is burned in unlined carbon steel, rotary burners or in spray-type burners. The sulphur dioxide gas is cooled in antimony lead or tellurium lead pipes submerged in water or over which water is allowed to flow. The lead is resistant to attack not only by sulphur dioxide and sulphurous acid but also by sulphuric acid, which is always formed to a small extent. A hard-lead fan blows the gas into the absorption towers. These towers are wood- or tile-lined concrete.

The gas passes to the towers, where it reacts with the limestone and water. The cooking liquor then formed is pumped by stainless-steel or bronze pumps through hard-lead or stainless lines to the accumulator of Type 317 stainless steel. Valves and fittings in contact with sulphurous acid are made of lead, bronze, or stainless steel.

SULPHONYL CHLORIDES

Sulphonyl chlorides have been used in the production of synthetic detergents and other products. Commercial production by the Reed method of preparing aliphatic sulphonyl chlorides by reacting saturated hydrocarbons with sulphur dioxide and chlorine under the influence of actinic light has taken place in the United States and Germany. (Lockwood, W. H., Hydrocarbon Sulphonation, *Chem. Ind.*, Vol. 62, No. 5, pp. 760–763, 1948.)

Production

Materials of Construction.—In the plant a reactor is used which is made from nickel or a nonferrous alloy of nickel, or it may be a glass-lined or chemical-stoneware vessel. It should be equipped with an agitator and either coils or a jacket for cooling. Means for supplying actinic light must be provided.

The Germans used a steel tower coated with a phenol-formaldehyde resin for a reactor. They used quartz tubes in the bottom of the tower and a mercury-vapor lamp. Mixed gases entered the bottom of the tower. The reaction mass was cooled by pumping the bottom portion through a heat exchanger and then into the top of the tower.

The phenolic resin protective coatings only lasted a few months and were replaced by a polyvinyl chloride coating, which is more satisfactory. Liquid sulphur dioxide was used to dissolve the sulphonyl chlorides from the unreacted hydrocarbons in the purification operation.

Process.—The hydrocarbon is put in the reactor, and a gaseous mixture of sulphur dioxide and chlorine is passed in until the mass has gained a predetermined weight. Cooling is necessary, since the process is exothermic.

The process can also be carried out continuously by passing the gases upward through a descending column of oil. The reaction with normally gaseous hydrocarbons such as propane and butane is carried out using a solvent such as carbon tetrachloride. The solvent is placed in the reactor, and the gaseous hydrocarbon is passed into the solvent simultaneously with the sulphur dioxide and chlorine. After the reaction the solvent is distilled off. The monosulphonyl chlorides can be removed by distillation under vacuum, and the disulphonyl chlorides can be crystallized from the residue.

SULPHUR

At the instigation of the Texas Gulf Sulphur Co., James R. West conducted an investigation to determine the present state of knowledge in regard to corrosion of sulphur and sulphide, especially molten and sulphur vapor. Below is a digest of the information obtained.

Handling

Aluminum.—All authorities agree that sulphur in liquid or vapor form does not attack aluminum. For example, laboratory data show that aluminum is not attacked by sulphur at 410 or 770°F. Aluminum has occasionally been recommended by its manufacturers for handling molten sulphur and sulphur vapor, and all reports on the resulting installations have been favorable.

Cast Iron and Steel.—The action of sulphur on steel is quite responsive to moisture, aeration, and temperature. Where all three of these factors are favorable, *i.e.*, where the molten sulphur is dry, unaerated, and at low temperature, steel and cast iron are suitable, but if any one of the three factors is unfavorable, excessive corrosion results.

Satisfactory service from iron and steel is recorded in a number of cases. Cast-iron pump parts were found suitable where operated submerged in molten sulphur at temperatures up to 350°F.; the original cast-iron seats in these pumps failed after 8 months' service, but the new stainless Type 312 seats failed in only a week, so that cast iron was again employed.

Liquid sulphur has been safely handled in tanks made of boiler-plate steel. The 1½-mile-long main sulphur lines at the mines of the Texas Gulf Sulphur Co. are standard black pipe, now twelve years old and apparently good for another twelve; their long life is attributed to the fact that no air, steam, or moisture is permitted to enter them.

Plain cast iron and mild steel can be used to handle solid and liquid sulphur at temperatures up to 350 to 400°F., provided air is excluded from the liquid and moisture from the solid. However, the temperature limit can be raised to 830°F. by metallizing with Cr or Al, and the ill effects of moisture relieved by the addition of ammonium bicarbonate to the solid sulphur.

Ceramics and Fused Silica.—It is reported that chemical stoneware in the usual applications is not heated above 300°F. and that, under these conditions, such stoneware is not attacked by sulphur, sulphides, or polysulphides. Silica shows toward sulphur its characteristic tendency to be rather inert.

Chromium.—Experience has disclosed that sulphur and sulphides do not have an appreciable effect on chromium. A great deal of chromium-plated equipment is installed under conditions where it is subjected to the action of elementary sulphur or sulphides, both plain and in aqueous solution, and at various temperatures, and in all cases the chromium has performed with commercial satisfaction. It is regrettable, however, that no quantitative data have been recorded on the rate of attack or nonattack by such compounds.

Copper.—Copper alloys are a lot better than copper itself, but they still leave much to be desired. It is reported that molten sulphur at 266 to 284°F., after 1 month, had tarnished Tobin bronze and had badly corroded brass. In tests conducted at 275°F. red brass and low brass were attacked the least; aluminum bronze, nickel, silver, and Muntz metal were almost as good; and Admiralty metal, aluminum brass, and silicon bronze were next in order. All were quite resistant compared with copper.

Magnesium.—Except for its comparatively low melting point (1203.8°F.) magnesium should be an excellent material for handling molten sulphur and sulphur vapor. The various references on this subject all agree that magnesium is inert to liquid or gaseous sulphur.

Nickel and Nickel Alloys.—If free access of air is prevented, nickel and Monel are quite resistant to corrosion by molten sulphur at temperatures up to 575°F. Above this temperature the corrosion rates increase sharply. The resistance of Inconel is reported good up to 690°F. Ni-Resist is no more resistant to corrosion by molten sulphur than plain cast iron. The effect of temperature on corrosion of nickel and its alloys is indicated in the following data. As the temperature of the molten sulphur was raised from 565 to 835°F., the corrosion rate of nickel went from 13 to 1,210 mils per year; Monel went from 36 to 1,300 mils per year; Inconel, the best of the lot, went from 0.8 to 36 mils per year; and Ni-Resist went from 131 to 592 mils per year.

There was no aeration in these tests; if air is present, all the nickel alloys show higher rates of corrosion at and near the liquid level. No evidence of embrittlement was detected in any of the materials tested.

Stainless Steel.—All the conventional chrome and chrome-nickel stainless steels resist liquid sulphur up to 400°F., though at temperatures that low ordinary steel and cast iron are resistant enough to put alloy steels at an economic disadvantage. Above 400°F. the stainless steels have better sulphur resistance than unalloyed steels, but there is considerable disagreement as to the exact and even the comparative resistance values offered by the several types of Cr and Cr-Ni alloy steels.

It is a fairly general consensus that, for service in liquid sulphur up to the boiling point, 17 per cent Cr steel or stabilized 18-8 stainless will probably be satisfactory but that operation at or above the boiling point, as in sulphur boiler tubes, requires higher alloys. For vapor service between the boiling point and about 1300°F., the controversy centers primarily around the 25 to 20 Cr-Ni alloy, straight 27 Cr steel, and an alloy containing 27 Cr and 2 or 3 Al. Any of these three could be expected to give adequate service, but no one of them has consistently proved best for all investigators. However, the preponderance of opinion, in point of corrosion resistance alone, seems to favor a high-chrome steel over a chrome-nickel steel and the Cr-Al steel over straight Cr. Unfortunately, high-chrome steels, and especially the Cr-Al steels, show a tendency toward increasing brittleness with alloy content.

Although the three steels above are mentioned most frequently for high-temperature resistance to sulphur, there are others that have been propounded. One containing Mo in addition to Cr and Ni and another with Mn and Cb as well as Cr have been recommended. Two rather special alloys, Illium G and Hastelloy C, have shown up well in tests.

Packaging

Sulphur is generally shipped in wooden or steel box cars, barges, or steamships. Sometimes open-top cars of steel are used.

In a short trial, aluminum freight cars were used to transport sulphur without revealing appreciable corrosion.

SULPHUR DIOXIDE

Sulphur dioxide is produced from several sources, sulphur, metal sulphides, and waste gases. The usual method for the manufacture is the burning of sulphur.

Production

Materials of Construction.—Dry gases can be handled in ordinary iron and steel. In the presence of moisture, more resistant materials are necessary. From the roasting of lead, zinc, and iron sulphides, large amounts of hot SO_2 vapors with other oxidation products are handled in lead ducts and in lead-lined equipment.

Process.—Sulphur can be stored out of doors on the ground or on a concrete-covered area. It is put into a concrete or steel tank and melted. The molten sulphur is pumped into the firebrick-lined furnace through a spray nozzle. Here it is burned with air to form sulphur dioxide. The gas is passed through a steel heat exchanger and pumped to absorbers. The strength of the solution from the absorbers is dependent upon the temperature and the strength of the entering gas, but the concentration usually runs from 1.3 to 2 per cent with the temperature close to 30°C. The gas next goes to the steaming tower and from it to the cooler. It is then dried in a tower with 98 per cent sulphuric acid. The sulphur dioxide is compressed, cooled, and stored.

Handling

Copper.—This metal is resistant to dry sulphur dioxide, in both the gaseous and liquid states. (Copper Development Association, "Copper in Chemical Plant," p. 12, London, 1936.) A protective covering of basic sulphate is formed when the sulphur dioxide is in a moist dilute state such as exists in industrial atmospheres. With concentrations appreciably higher than this, resistance depends to a large extent on the particular conditions. Thus in the presence of water and air, sulphuric acid may be formed in a concentration sufficient to cause severe corrosion. Flue gases, whether from solid, liquid, or gaseous fuel, always contain sulphur oxides and oxygen, but the corrosion resistance of copper is usually adequate in these cases, as condensing conditions rarely obtain.

Worthite.—Wet sulphur dioxide gas and sulphurous acid conditions are nearly identical in their corrosive effect on chrome-nickel-moly and nickel-chrome-moly alloys. (Pratt, W. E., Worthite, *Chem. Eng.*, Vol. 54, No. 7, p. 221, 1947.) Theoretically, the wet SO_2 gas should be less corrosive to these types of alloys owing to the probability of the environment's having more oxidizing capacity. The opposite would be true when bronzes or nickel-copper alloys are involved.

Stainless alloys of the 18-8S Mo type (Type 316 or 317) have been considered for some time as acceptable alloys for SO_2 and H_2SO_4 conditions in the sulphite pulp and paper industry. The higher alloyed nickel-chrome-moly alloys such as Worthite have proved more useful when some sulphuric acid is present. If a film of sulphurous acid is left on a surface under shutdown conditions, it is possible, with air present, for some oxidation to take place and form H_2SO_4. At the high temperatures encountered in SO_2 cooler pipes or water spray pipes used for cooling the SO_2 gas from 1100 to approximately 400°F., Worthite has proved to be superior to the regular chrome-nickel-moly stainless steels.

Worthite sulphurous acid tower circulating pumps have shown good performance records for a long period of years, requiring no repairs. Installed with independent water seals on the stuffing boxes, the pumps require repacking only at general overhauling periods or otherwise not more frequently than about once a year. Worthite pumps in service since 1936 handling 1.05 sp. gr. H_2SO_4 show no signs of corrosion.

Scrubber gas effluent contains appreciable percentages of SO_2 or H_2SO_4. A test was made of a large public-utility company on Worthite in this effluent for a period of 20 months. The loss of weight was reported as only 0.75 per cent, or practically nothing. Where smelter gas is used for the manufacture of sulphuric acid (instead of burning sulphur or pyrites), that gas is usually passed through scrubbers to remove flue dust. The scrubbers are usually of lead construction, and Worthite pumps have been used successfully in circulating water over the scrubber. The pump therefore has to handle a hot, weak sulphurous acid solution containing appreciable percentages of solids. Subsequently the SO_2 gas is dried by passing through a tower over which a Worthite pump circulates concentrated sulphuric acid, which becomes saturated with the SO_2. No discernible corrosion or wear has been reported on such application of Worthite pumps.

Nickel.—Nickel and Monel are resistant to dry sulphur dioxide at temperatures up to about 600°F. (Friend, W. Z., Nickel, Nickel Alloys, *Chem. Eng.*, Vol. 54, No. 7, p. 222, 1947.) Above this temperature these materials are subject to intergranular sulphur attack, which results in embrittlement. Inconel is resistant up to about 1500°F. The upper temperature limit for Ni-Resist has not been established. These limits apply also to wet sulphur dioxide gas, where temperatures are always well above the dew point of the sulphur dioxide–water mixture. Monel is used for valve and pump parts and miscellaneous fittings in handling anhydrous sulphur dioxide in the refrigeration and other industries.

Type 1 Ni-Resist has been used for gas manifolds and distributors carrying hot mixed gases from sulphur burners to coolers in sulphite pulp mills.

None of these materials is resistant to wet sulphur dioxide at temperatures below the dew point of the sulphur dioxide–water mixture or in continuous exposure to sulphurous acid solutions containing more than about 0.3 per cent SO_2 by weight. There are numerous applications, such as in the handling of fruit juices and food products containing sulphur dioxide as preservative and in the handling of such solutions as steep water and gluten water in corn-products plants, where SO_2 contents are low enough so that Monel, nickel, and Inconel have good corrosion resistance. In some cases Monel and nickel may show a superficial tarnishing owing to SO_2 content. Inconel is superior in this respect.

Monel, nickel, Inconel, and Ni-Resist are not resistant to the strong sulphite liquors encountered in the acid plants, digesters, and blow pits of sulphite pulp mills. Ni-Resist has been used to some extent for blow-pit pipes. All these materials have given good performance in handling the washed pulp after discharge from the blow pit. Monel, in particular, is used for such equipment as rotary pulp screens, thickeners, and washers. Ni-Resist is used for pumps, valves, pipe, and fittings handling washed pulp and white water.

Silicones.—Silicones in their various forms have been exposed to wet and dry sulphur dioxide at atmospheric pressures and to sulphurous acid at room temperature for 2 weeks in order to determine their stability to these reagents. (McHard, J. A., Silicones, *Chem. Eng.*, Vol. 54, No. 7, p. 224, 1947.) In general, the resistance of various silicone products to both wet and dry sulphur dioxide is good. With the exception of the silicone resins and certain Silastic stocks, the resistance of silicones to sulphurous acid ranges from fair to poor. Three silicone resins were exposed to both wet and dry sulphur dioxide and to sulphurous acid and found to be relatively unaffected.

In general, the stability of Silastic stocks to wet and dry sulphur dioxide ranges from fair to good. The resistance of most stocks to sulphurous acid is generally poor, with the exception that Silastic 120 appeared to be somewhat improved.

Rubber.—While rubber-lined tanks, pipes, and fittings have not found extensive application in SO_2 services, specific compounds of hard rubber have excellent resistance to sulphurous acid up to saturation at atmospheric pressure and at temperatures up to 150°F. (True, O. S., Rubber Linings, *Chem. Eng.*, Vol. 54, No. 8, p. 209, 1947.) Soft rubber cannot be recommended for SO_2 because of the high rate of diffusion of this gas through such compounds. This diffusion results in failure of the rubber-to-metal bond with subsequent blistering of the lining away from the metal.

Laboratory investigations at atmospheric pressure and temperature of the effects of wet and dry SO_2 have been conducted on natural rubber and all the synthetics. Results obtained indicate that the gas has a more serious effect on soft and semihard rubbers than does sulphurous acid. The semihard rubbers are softened appreciably by absorption of the gas. The soft rubbers with the exception of GR-I (butyl) are rapidly diffused and blistered under these conditions. It is likely that GR-I could be used to good advantage in SO_2 service, since it has exceptional resistance to gas diffusion. Actual rate of diffusion of SO_2 through this material has not been determined, but the exposure tests described above indicated excellent resistance to both solution of and permeation or diffusion by the gas. Within the limits of the tests, none of the other synthetic rubbers showed advantages over hard natural rubber.

Durimets.—Dry SO_2 gas is handled very readily in cast iron and other such materials. In the presence of moisture, more resistant materials are indicated. (Watkins, W. A., Durimet T and 20, *Chem. Eng.*, Vol. 54, No. 8, p. 209, 1947.) Durimet is being used successfully under moist SO_2 gas conditions at temperatures up to 900°F. In general, however, the top limit for continuous high-temperature operation would be about 800°F.

Durimets T and 20 are available as engineered process equipment and special castings. The former includes centrifugal pumps, valves, pipe fittings, steam jets, and exhaust fans. Durimet T only is obtainable as cold-finished round bar.

Durimet equipment is being used in the following typical industrial applications:

1. Durimet-T centrifugal pumps for tower circulation and transfer service in sulphite pulp mills.
2. Durimet T fan handling dry 10 per cent SO_2 gas to 230°F.
3. Durimet spray nozzles in SO_2 gas cooling and scrubbing towers. Gas temperature is 750 to 900°F. with cooling water at 125°F.; weak H_2SO_4 formed owing to SO_2 in burner gas.
4. Durimet T fan runner delivering approximately 14½ per cent SO_2 gas at 75 to 85°F. with occasional traces of sulphuric acid due to SO_3 gas and moisture present.
5. Durimet T manhole sleeves, steam coil sleeves, blowoff connections, etc., on Mitscherlich digesters in sulphite mill. Sulphurous content is as high as 6 per cent at temperature of 275°F.
6. Durimet top and bottom fittings such as liner sleeves, relief strainers, cover liners, valves, and blowoff crosses for vertical sulphite digesters.
7. Durimet target plates for protecting walls of blow pits in sulphite pulp mills.

The high-silicon irons, Duriron and Durichlor, are not recommended for handling sulphur dioxide or sulphurous acid. The same holds true for Chlorimet 2 and Chlorimet 3.

Aluminum.—Because of its excellent resistance to attack by sulphur and sulphur products, aluminum has come into wide use for handling elemental sulphur, sulphur dioxide, hydrogen sulphide, sulphurous acid, and fuming sulphuric acid. (Verink, E. D., R. H. Wagner, and R. H. Brown, Aluminum, *Chem. Eng.*, Vol. 54, No. 8, p. 210, 1947.)

Refrigerating engineers have long recommended the use of aluminum for refrigerating systems wherein sulphur dioxide was the refrigerant as well as for systems utilizing the Freons and methyl formate. Aluminum has also demonstrated its ability to withstand the corrosive conditions encountered in sulphur dioxide towers used in the refining of corn products.

Aluminum alloys are resistant to moist sulphur dioxide and its dilute solutions in the absence of chlorides and heavy metals.

Protective Coatings.—Plant exposure conditions have indicated that Prufcoat has stood up well under fairly strong concentrations of sulphur dioxide. (Anon., Protective Coatings, *Chem. Eng.*, Vol. 54, No. 8, p. 214, 1947.) In general, the phenol-formaldehyde resins, polyvinyl chlorides, polyvinylidene chlorides, Thiokol, neoprene, and rubber-base materials have good resistance. Heresite is good up to 175°F.; Heresite AD 640, a vinyl resin, is recommended up to 100°F. Amercoat is said to be unaffected by sulphur dioxide. Fedelco was tested under varying concentrations for 18 months and gave good results. Quigley Black is not affected. Triple A Nos. 10 and 20 are not affected by SO_2 gas.

Haveg.—Haveg equipment has an excellent service record under all operating conditions involving sulphur dioxide that come within the physical limitations of a plastic material. (Mampe, E. P., Haveg, *Chem. Eng.*, Vol. 54, No. 9, p. 209, 1947.) It has been used with complete success under a wide variety of conditions of temperature, concentration, moisture, and pressure with sulphur dioxide both alone and in combination with other chemicals. Haveg 41 has been used over a period of 14 years without showing any evidence of attack due to wet or dry sulphur dioxide or sulphurous acid in such equipment as fume ducts, pipe and fittings, jets, cooler manifolds, and tanks.

Haveg 60, although of more recent origin, also has proved to be equally resistant.

Lead.—Since 1746, when the first lead chamber was used in Birmingham, England, for making oleum, lead has proved its worth in handling sulphur dioxide and related compounds, such as sulphuric acid, sulphurous acid, sulphur chloride, and sulphur trioxide. (Church, H. M., Jr., Lead, *Chem. Eng.*, Vol. 54, No. 9, p. 209, 1947.) Lead suffers practically no corrosive effects from SO_2 gas, whether cold and dry or in hot, moist condition up to 390°F. In fact, lead is a standard material for handling the above corrosives.

From the roasting of lead, zinc, and iron sulphides large amounts of hot SO_2 vapors with other oxidation products are handled in lead ducts and in lead-lined equipment. The actual conversion of the SO_2 to concentrated sulphuric acid is accomplished by the contact process, but extensive use of sheet lead is made in the purification of the hot gas coming from the roasters prior to its conversion.

In the manufacture and handling of sulphurous acid for the sulphite paper process lead has many uses. The hot SO_2 gas is taken through a cooling system which usually consists of 100 or 200 ft. of 8- or 12-in. lead pipe undergoing a continuous cold-water spray. Lead fans impel the gas countercurrent to a water stream through limestone-packed towers to form the sulphite liquor, which usually contains 1 per cent SO_2 combined with lime and 5 per cent free SO_2. Sulphite liquor and wood chips are brought into a digester with a lining of acid-proof brick set in a cement made of litharge (PbO), sand, and glycerin. Here temperatures vary from 250 to 300°F., and pressures are 75 to 125 psi. At the digester top 1-in. antimonial lead covers, 36 in. in diameter, have given good service at 250°F. at 20 per cent of the cost of covers previously used.

Tantalum.—Under most circumstances, there are so many materials resistant to wet or dry SO_2 or sulphurous acid that the use of tantalum, because of its relatively high cost, is not necessary. (Hunter, F. L., Tantalum, *Chem. Eng.*, Vol. 54, No. 9, p. 210, 1947.)

Tantalum is completely immune to sulphurous acid at any concentration or temperature in the liquid phase and to sulphurous acid vapors or dry SO_2 at temperatures up to 350°C., provided that no free SO_3 is formed by catalytic or other action. If there is evidence or probability of the formation of SO_3 during the reaction, tantalum should be tested under the actual operating conditions before deciding on its use.

There are certain conditions, especially when it is contaminated with other materials, when sulphurous acid can be extremely corrosive. Likewise, sulphur dioxide or sulphurous acid can become a troublesome component in food, drug, or fine-chemical products where, by corrosive action on the equipment, it causes contamination of the product. Under such conditions, where common materials of construction fail, tantalum can be used economically for heaters, coolers, condensers, diaphragms, thermometer wells, or other vital parts.

Hastelloy.—Wet and dry sulphur dioxide gas is usually present in flues and furnace atmospheres when sulphur dioxide is a product of combustion. (Chisholm, C. G., Hastelloy, *Chem. Eng.*, Vol. 54, No. 9, p. 212, 1947.) Temperature and moisture conditions have considerable bearing on the corrosion rates of this gas coming in contact with the alloys. In general, high-chrome or chrome-nickel steels successfully resist the flue gases and furnace atmospheres, the amount of chrome or chrome-nickel depending upon the temperature.

Hastelloys A and B resist wet and dry sulphur dioxide gas effectively but only at temperatures up to 1400°F. Hastelloy C, however, resists this gas at temperatures up to 2000°F. because of its chromium content and superior oxidation resistance. For this type of service Hastelloys should, in general, be used only on those parts which must withstand severe stresses. For straight oxidation resistance and resistance to the corrosive attack of sulphur dioxide gas, wet or dry, the superiority of Hastelloys is not sufficient to justify the use of these higher priced alloys instead of high-alloy stainless steels. The superior strength of these alloys at higher temperatures, however, makes their use for highly stressed parts particularly satisfactory from the standpoint of long life and resultant economies. The ultimate tensile strength of Hastelloy alloy is in excess of 60,000 psi. at 1500°F.

Stainless Steel.—Stainless steel provides valuable corrosion resistance in many applications where sulphur dioxide, sulphurous acid, or solutions of these agents are encountered. (Anon., Stainless Steel, *Chem. Eng.*, Vol. 54, No. 9, p. 214, 1947.) It is especially valuable in the pulpmaking industry, where sulphite acid liquors containing free sulphur dioxide and an excess of sulphurous acid must be handled in equipment including heat exchangers, digester circulating systems, digester relief lines, steam injectors, various tank linings, tie rods, and other related installations. Stainless steel is used also for reaction vessels for combining SO_2 with other substances, for SO_2 absorbers, and for tanks to hold liquids containing SO_2 in solution. Dry gaseous SO_2 and combustion products containing SO_2 are conveyed in tubes, exhaust pipes, flues for roasting furnaces, and stacks for burners using fuel oil or industrial fuel gases.

Stainless steels Types 304, 308, 316, 317, and 329 have been widely used in the sulphite pulp industry. Of this group, Types 316 and 317 are preferred for heat exchangers, digester circulating systems, and relief lines which are exposed to the liquors containing sulphuric and sulphurous acids formed by the combination of sulphur dioxide and water. Where the corrosive conditions are less severe, as in steam injectors and blow-pit linings, Types 308, 329, and in certain instances even 304 can be used.

Liquids such as processed fruit juices containing small percentages of SO_2 completely in solution as a preservative are safely stored in tanks made of Type 302 or 304. However, if the saturation limit of the liquid is exceeded in closed tanks, corrosion may occur above the liquid level. Types 316 and 317 pipe lines, valves, and pump parts provide good service for handling sulphurous acid and solutions containing SO_2.

Type 316 units are suitable for the manufacture of chemical compounds such as sodium bisulphite, which is made by bubbling SO_2 through a mixture of soda ash and water, provided that vapors are not enclosed above the liquid level.

Absorbers made of Types 316 and 317 have given satisfactory performance for collecting wet SO_2 gas when operated under properly controlled conditions.

The stainless steels are highly resistant to dry SO_2 at temperatures as high as 1200°F., but the rate of attack increases appreciably upon further elevation of temperature. If moisture is present and condensation of the vapor occurs in the lower temperature ranges, the severity of corrosive attack will depend upon the extent of condensation and other operating conditions.

Types 430 and 316 afford long service life in commercial equipment for handling combustion products containing SO_2. Corrosion in such applications is encountered chiefly in the presence of condensed moisture, which permits the formation of mixtures of sulphurous and sulphuric acids. Type 430 is used for parts of stacks and flues that are subject to operating temperatures above 800°F. where condensation does not occur. Type 316, which is more resistant to sulphurous acid and weak sulphuric acid, is used for the cooler sections of the equipment.

Many of the corrosion problems associated with SO_2 and sulphurous acid applications arise from the incidental formation of more corrosive substances due to certain operating conditions as discussed above. Competent technical advice often can eliminate such difficulties prior to installation.

Glass-lined Steel.—This material is totally unaffected by SO_2 and can be used up to 500°F.

Stoneware.—Chemical stoneware is inert to both wet and dry SO_2 and sulphurous acid at all concentrations and all temperatures at which stoneware is commonly used. (Herstein, F. E., Chemical Stoneware, *Chem. Eng.*, Vol. 54, No. 9, p. 216, 1947.) Its use in handling of these materials is therefore limited only by economic considerations and the extent of thermal shock prevalent in any particular installation.

One of the widest uses of chemical stoneware in connection with SO_2 and sulphurous acid is in the absorption of SO_2 to form sulphurous acid. Chemical-stoneware towers up to 48 in. diameter and as high as 35 or 40 ft. are used for this purpose. The packing material for these towers is usually chemical-stoneware rings. The piping, circulating sumps, pumps, and other accessories for an SO_2 absorption system can also be made of stoneware.

Besides the application mentioned above, chemical stoneware can also be used for any other handling operation involving SO_2 and sulphurous acid at temperatures below 220°F. Where sulphurous acid is used as an antichlor in textile plants, stoneware piping and pumps are used for handling.

Wood.—The following service data for tanks used in sulphite mills may be helpful. This information was supplied by sulphite mill operators and is believed to be typical of the industry. (Chaney, S. E., Wood Tanks, *Chem. Eng.*, Vol. 54, No. 9, p. 218, 1947.)

Wood tanks are used almost universally for the storage of raw sulphite acid. The concentration of the acid is 4 to 5 per cent total sulphur dioxide with 1 to 1.5 per cent combined sulphur dioxide. The temperature is generally 15 to 20°C. The life of these tanks is 10 to 15 years; some have been known to last longer.

Wood tanks are also used as reclaimed or cooking-acid storage tanks. The concentration of the acid may be 5 to 6 per cent total; temperature will range from 30 to 40°C. or above. When the temperature is above 40°C., the life may be 5 to 7 years. When the temperature is below 35°C., then the life of the tanks may be 10 to 14 years.

Wood tanks with tile lining are generally used for temperatures above 40°C. The wood tanks are of the same general size as indicated for the raw-acid tanks.

One pulp and paper plant operator reports having three 12- by 25-ft. tanks made of southern yellow pine 6 in. thick in use for the storage of sulphite cooking acid. Strength is 4.85 per cent total, 2.0 per cent combined. The temperature is 86°F. These tanks have been in service for 12 years and at present are in a good condition.

Another common use of woods in the sulphite mill is in the blow pits. These tanks are subjected to relatively weak sulphite acid solutions for a short period of time. Thus, their life may be 20 years. Decay from the outside may do more damage than chemicals within. The ducts from the blow pits to the vomit stacks and the vomit stacks themselves are usually made from wood. These constructions are subject to the action of moist, dilute sulphur dioxide, and life is 15 to 20 years. The damage, if any, may be due to dilute sulphuric acid formed from the sulphur dioxide under the moist, oxidizing condition. Dry sulphur dioxide gas is not encountered in a sulphite mill, although wooden construction would be expected to be resistant to this chemical.

Carbon and Graphite.—There is no evidence of corrosion of either carbon or graphite by sulphurous acid or by sulphur dioxide in any concentration below its dissociation temperature. In those cases where SO_2 is associated with free SO_3, or with air at temperatures exceeding 610 or 800°F., carbon and graphite, respectively, may be expected to react as they would with those reagents alone. (Werking, L. C., Carbon and Graphite, *Chem. Eng.*, Vol. 54, No. 9, p. 222, 1947.)

The corrosion characteristics of Karbate products are similarly within the operating temperature limitation, 340°F., of the material itself.

Outstanding evidence is to be found in the use of carbon and graphite elements in wet flue-gas scrubbers for powdered fuel boilers, where, after approximately 10 years of service, no corrosion has been found in spite of conditions varying from dry to water saturation and the presence of air and combustion gases. Over periods of years no attack is evident in calcium bisulphite solutions saturated with SO_2 (sulphite liquor in paper mills) at temperatures to 300°F. Graphite bubble caps and trays are used in columns handling SO_2 plus low concentrations of H_2SO_4 subject to occasional neutralization by sodium hydroxide. Porous carbon is used for the dispersion of SO_2 containing low concentrations of SO_3.

For all practical purposes, carbon, graphite, and Karbate can be used as or in all types of equipment subject to sulphur dioxide and sulphurous acid in all concentrations without fear of corrosion.

Glass-lined Steel.—Standard glass-lined steel reactors are used for reactions involving sulphur dioxide gas, wet or dry, and sulphurous acid with satisfactory results and service life. (Chormann, O. I., Glass-lined Steel, *Chem. Eng.*, Vol. 54, No. 9, p. 224, 1947.)

Packaging

Sulphur dioxide is shipped as a liquid in steel cylinders, in 1-ton tanks, and in steel 15-ton tank cars.

SULPHUR DIOXIDE—PHENOL

A system of siphon lines which carry filtrate water containing sulphur dioxide and phenol uses 200 ft. of 2-in. Saran pipe. A 10-lb. head of steam is used to force this water into storage tanks. This results in the lines being subjected to steam at 200°F. for a few minutes after each run of water is completed. Copper tubing was used in this line previously and lasted about one year. The present Saran line has been in operation for some time and shows no deterioration. (Williams, D. R., Properties and Applications of Saran Pipe, *Chem. & Met. Eng.*, Vol. 52, No. 11, pp. 112–113, 1945.)

SULPHURIC ACID

Aside from the large tonnage of sulphuric acid produced and the problem of designing plant equipment used for this production, the acid is generally a factor in considering plant equipment for many other processes. Since, in general, the same principles that govern the selection of material for handling sulphuric acid in process of manufacture can be applied in designing equipment for processes in which this acid is an essential raw material, a discussion of sulphuric acid-manufacturing equipment will serve as a manual for other process plants.

This important acid flows into the chemical industry from several sources, including contact catalysis and lead-chamber manufacture, recovery of spent mixed acids and waste materials, or concentration of weak solutions to more usable strength. In the contact plant a generally higher concentration range has to be handled and the problem of selecting material for the higher concentration range is relatively simple. The range of concentration is from about 90 to 109 per cent, and the temperature may reach as high as 250°F.

Usually in contact manufacture the raw materials are sulphur and air. The intermediate ingredients that have to be handled at certain stages of the process are SO_2 and SO_3, both wet and dry. These two gases are present under temperatures as high as 1900°F. Probably the most difficult problem lies in their handling, but the corrosion can be controlled largely by regulation of the moisture content. Assuming proper control, the materials used can be iron and steel, as in most of the equipment in the contact plant.

Probably the greatest corrosion by sulphuric acid is encountered in the recovery and concentration plants. Sulphuric acid is peculiar in that the greatest corrosion of material occurs in the lower and upper ranges of concentration, and the most severe range is between 75 and 85 per cent H_2SO_4. The recovery and concentration of the acid involves the handling of concentrations from 50 to 93 per cent. (Huey, W. R., *Chem. & Met. Eng.*, Vol. 36, No. 9, p. 573, 1929.)

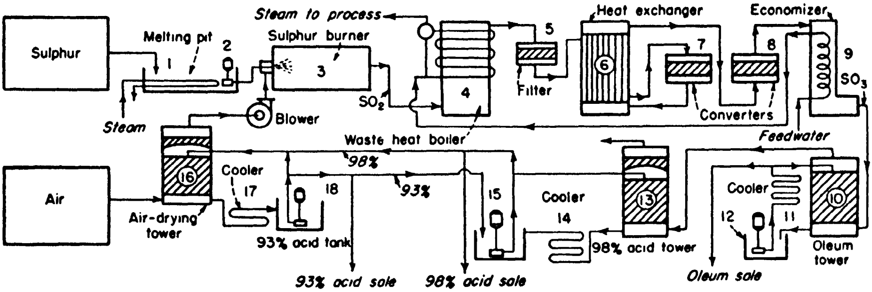
Production

Materials of Construction (Contact Process).—The author recently visited the contact acid plant of Naco Fertilizer Co. at Charleston, S.C. It had been completed only a few months previously and can be considered more or less typical of present-day contact plants. In general, the construction was plain iron or steel; however, a few pieces of equipment had been made of other materials.

Materials of Construction (Lead Chamber).—In the lead-chamber plant the concentration of H_2SO_4 seldom exceeds about 60°Bé. Aside from the corrosive nature of the low-strength sulphuric acid, the problem of selecting materials is further complicated by the presence of oxides of nitrogen at certain stages in the process. Chemical lead and acidproof stoneware are the materials that are most satisfactorily used in this case.

Contact Acid Process.—Sulphur is melted in a concrete or steel pit. After impurities have settled out, the sulphur is pumped into the brick-lined furnace through a spray nozzle. One large plant utilizes Durimet 20 pumps for the molten sulphur and finds it to be better than cast iron or steel ordinarily used. Here it is burned in predried air to form sulphur dioxide. The air for combustion is drawn from the atmosphere through a filter into the brick-lined steel drying tower. Strong acid (93 per cent) is circulated over the brickwork in this tower and removes the moisture in the air. Heat generated by dilution of acid with water vapor is removed in cast-iron cooler sections. Acid is pumped over the drying tower and through the coolers by a La Bour pump (impellers of R-55 alloy).

Hot gases leaving the sulphur furnace pass through a waste-heat boiler in which they are cooled. After being filtered in a tray gas filter, where ash is removed, the gas enters heat exchangers. Here the temperature is raised to the required point for the first layer of catalyst mass. During this heating operation, the temperature of the gas entering the secondary converter is also cooled. Gas passes through two layers of mass in the primary converter, where partial conversion from SO_2 to SO_3 takes place. It is then cooled in the heat exchanger



Sulphuric acid (contact process, raw gas–brimstone plant, vanadium catalyst).

1. Steel or cement-brick lined
2. Cast iron and steel
3. Steel, firebrick-lined
4. Steel, firebrick
5. Steel
6. Steel
7. Steel
8. Steel
9. Steel, firebrick
10. Steel, acidproof-masonry-lined
11. Steel
12. Steel, acidproof-masonry-lined
13. Steel, acidproof-masonry-lined
14. Cast iron
15. Steel, acidproof-masonry-lined
16. Steel, acidproof-masonry-lined
17. Steel, acidproof-masonry-lined
18. Steel, acidproof-masonry-lined
19. Cast iron and steel

Pumps: cast iron and alloy
93% and 98% acid lines: cast iron
Oleum acid lines: steel
Valves: Aloyco 20

before entering the secondary converter. Further conversion takes place. The gas is further cooled before it enters the last layer of mass.

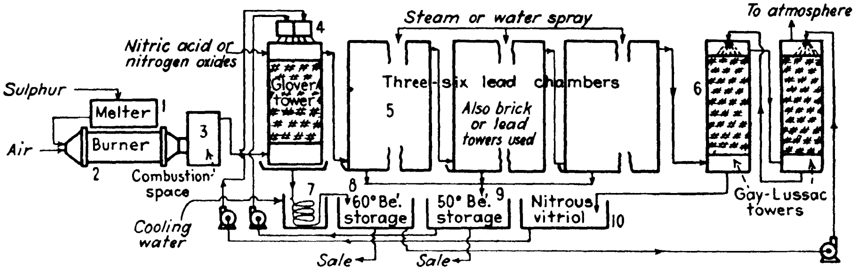
Hot gases leaving the converter are cooled before entering the absorption tower. This cooling is done in an economizer. Gas leaves the economizer at 450°F.

The SO_3 is removed from the gases by scrubbing with 98 to 99 per cent acid in a tower similar to the drying tower. Heat generated is removed by cooling the circulating acid in cast-iron cooling sections. Acid is pumped over the tower and through the coolers by means of an acid pump (with impellers of R-55 alloy). Valves in the 98 per cent acid line are special alloy. Durimet 20 valves are used widely in contact plants. In fact, several plants use these valves exclusively.

Either 93 or 98 per cent acid is withdrawn and diluted with water to 60°Bé. Since a large amount of heat is generated when diluting in this range, coolers and circulating pumps are provided to remove this heat. The cooler sections are made of cast iron and should not be used to provide acid of lower strengths than 60°Bé., since lower strengths would cause excessive corrosion. Acid is pumped to a large steel storage tank. From here it is handled by Durimet 20 and high-silicon iron pumps.

Acid for use in making the superphosphate is pumped by this same high-alloy steel pump to lead-lined acid-brick tanks mounted on concrete. It is conveyed to the chemical plant in lead lines for use in other processes.

Lead-chamber Process.—A lead-chamber plant is vastly different. From bins, sulphur is discharged by gravity into hoppers attached to the steel burners and is fed by worm feeders into the latter. The hot gases are conducted through a masonry combustion chamber. Sufficient oxides of nitrogen, NO, and NO_2, are introduced into the hot mixture of air and sulphur dioxide from the burner. The combustion chambers are equipped with automatic valves for regulating the intake of secondary air supply, controlled by gas analyzers, and by this means the fluctuations in sulphur dioxide percentage in the gas entering the Glover towers are limited to a range of 0.5 per cent.



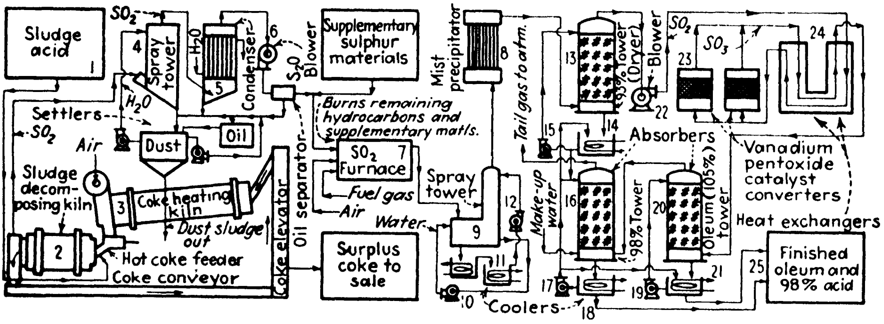
Sulphuric acid (chamber process).

1. Steel
2. Steel
3. Brick-lined
4. Brick, chemical-lead parts, stoneware packing
5. Chemical lead
6. Chemical-lead parts, stoneware packing
7. Chemical lead
8. Chemical lead
9. Chemical lead
10. Chemical lead

Pumps: hard or chemical lead
Blower: hard or chemical lead

The hot gaseous mixture passes up the radial-brick Glover tower, where it is met by the downward flow of the diluted Gay-Lussac acid. In the Glover tower about 10 per cent of the acid is formed. If an ammonia-oxidation unit supplies the nitrogen oxide, this is preferably entered into the gas stream after the gas has been cooled by its passage up the Glover tower. Cooled gases are blown to the chemical lead chambers, where most of the acid is produced and condensed. Finally, the reacted gases pass to the masonry Gay-Lussac tower for the adsorption of the oxides of nitrogen in the strong Glover acid, producing the Gay-Lussac acid. Chemical lead is also used for pans and curtain walls of Glover and Gay-Lussac towers.

Recovery and Concentration.—In some industries such as petroleum refining, nitric acid, rayon, chlorine, and alcohols, a large portion of the sulphuric acid can be reclaimed and used over again after concentration and in some cases purification. Many processes result in spent acids which can be reclaimed. These different kinds of acid vary in acidity and contain impurities such as hydrocarbons or sulphates. Composition of the acid together with the desired acidity after concentration will determine which method of concentration is best suited. Several different processes are on the market.



Sulphuric acid from refinery sludge (Chemico sludge conversion process).

1. Carbon steel
2. Carbon steel, brick-lined
3. Carbon steel, brick-lined
4. Carbon steel, lead-lined
5. Carbon steel, lead-lined
6. Aloyco 20
7. Carbon steel, firebrick-lined
8. Carbon steel, lead-lined
9. Carbon steel, lead- and brick-lined
10. Aloyco 20
11. Carbon steel, lead lining, lead coils
12. Aloyco 20
13. Carbon steel, brick-lined
14. Cast-iron cooling section
15. Cast iron
16. Carbon steel, brick-lined
17. Cast iron
18. Cast-iron cooling section
19. Steel
20. Carbon steel, brick-lined
21. Steel cooling section
22. Carbon steel
23. Carbon steel
24. Carbon steel
25. Carbon steel

Piping: Cast iron for 80 to 99 per cent H_2SO_4; steel for 99 to 109 per cent; lead for acid under 80 per cent
Valves: Aloyco 20

Simonson-Mantius Process.—This process depends upon concentration of acid under vacuum. There are five general types of concentrators. Briefly, they vary in arrangement and type of heating elements, also in respect to maximum heating surface and range of acidities. Type A is used for continuous evaporation of large volumes of water at acidities below 45 per cent. Type B is for medium acidities of from 25 to 75 per cent. Type E, the most generally used concentrator, is for concentrating from any low acidity up to 95 per cent. This type can also be used in cases where solids are precipitated during concentration of the acid. Type C is a concentrator having numerous small compartments. Type D differs only slightly from Type E. Materials of construction for the Simonson-Mantius units were discussed in a paper before A.I.M.E. (Burke, J. F., and E. Mantius, *Chem. Eng. Progress,* Vol. 43, No. 5, p. 239, 1947.)

Falling-film Process.—The Du Pont falling-film process was developed to provide equipment of moderate capacity (40 to 50 net tons per day) which would tie in readily with other acid operations, require minimum maintenance, employ available power facilities, and involve no fumes. Vacuum falling-film tube design accomplished the above objective and, in addition, provided a concentrator which does not require the use of large corrosion-resistant process vessels. High-silicon iron tubes are used in this process.

Concentration of sulphuric acid in the Du Pont falling-film unit is continuous, very little acid being retained in the equipment. (Chamber, F. S., and R. F. Peterson, *Chem. Eng. Progress,* Vol. 43, No. 5, p. 219, 1947.) The unit comprises (1) a preheater consisting of jacketed high-silicon iron tubes, (2) 4-ft.-diameter separating and distributing tanks constructed of lead-lined steel, (3) a barometric condenser supplemented by a two-stage steam ejector for removal of noncondensable gases, and (4) the four jacketed high-silicon iron falling-film tubes to which are attached lead outlet cooling pipes.

With this arrangement, the lead-lined equipment is in contact only with weak acid at its vacuum boiling point, and surfaces exposed to hot strong acid are high-silicon iron, which exhibits excellent corrosion resistance under these conditions. While operating experience is based largely on the use of high-silicon irons, other suitably resistant alloys, such as high-silicon nickel, can be used.

The process involves preheating to as high a temperature as possible followed by partial concentration, which results when the hot acid enters the vacuum system. The main concentration, however, occurs beyond this point when the so-called "flashed" acid at its vacuum boiling point is caused to flow over the upper ends of the vertical steam-jacketed tubes and pass down the inside surface as a falling film. To utilize steam as a heating medium the system is operated at an absolute pressure of about 25 mm. Hg.

Drum Concentrator.—Many units of this type have been installed for recovery of acid used in various branches of the chemical industry or for production of 66°Bé. (93.2 per cent) acid from 60°Bé. (77 per cent) chamber acid.

As now designed, the drum concentrator consists of three separate cylindrical steel shell vessels capable of a variety of arrangements in juxtaposition but generally arranged in line. (Berger, J. H., and A. J. Gloster, Chemico Drum Type Sulphuric Acid Concentrator, *Chem. Eng. Progress,* Vol. 43, No. 5, pp. 225–227, 1947.) In the first vessel, called the "combustion furnace," which is lined with insulating firebrick, oil or gas is burned with air supplied under forced draft by a centrifugal blower. Hot gases leave the furnace at 1100°F. and enter the second vessel, the concentrating drum, which is divided into two compartments and is lined with heavy sheet lead and 12 in. of acidproof masonry. The cast iron and acidproof iron gas piping is arranged so that, by proper control of dampers, hot gases from the combustion furnace can be delivered to each compartment in the proportions desired and released beneath the surface of the acid.

Under normal operating conditions, part of the hot gases enter the "high-stage" compartment in which strong (93 to 96 per cent) acid is produced and leave at 440 to 475°F. depending upon the strength of acid made. These gases are then released beneath the surface of the acid in the second, or "low-stage," compartment, and additional water is evaporated so that the gases leave this compartment at 340 to 360°F. depending on the average strength of the acid at this stage of the concentration. They then enter the third vessel, the "cooling drum," which is also lined with lead and acidproof masonry, where they impinge on the surface of the acid, preheat it to the boiling point, and leave at a temperature of 230 to 260°F. depending on the concentration of the feed acid. Spent gases go to a scrubbing tower or, more generally, to an electric mist precipitator for the removal of H_2SO_4 mist.

Feed acid is delivered to the cooling drum by pumps or air lifts, whence it flows by gravity countercurrent to the flow of gases. Product acid leaving the high-stage compartment passes through an acid cooler before going to storage. Acid is transferred from stage to stage in luted acidproof iron pipes.

Handling

Cast Iron and Steel.—These materials are extensively used in sulphuric acid service for concentrations from about 80 up to and including 100 per cent. With concentrations over 98 per cent and temperatures up to 140°F., steel is recommended for tanks and piping. For valves and pumps where the velocities are high, chrome-nickel alloys are more satisfactory. In the range between 100 and 102 per cent, neither cast iron nor steel is serviceable. Above 102 per cent, steel is satisfactory with the same exceptions as between 98 and 100 per cent. Where the concentration is between 90 and 98 per cent, steel is recommended for tanks and cast iron for pumps and valves at temperatures up to the boiling point. Both can be used for piping, although cast iron is preferred at the high temperatures. Cast iron is not used in some plants because of safety considerations.

In the concentrations between 80 and 90 per cent at atmospheric temperatures, cast iron and steel are both reasonably serviceable for the various uses, although the corrosion is greater in this range than it is for the higher concentrations. For valves much below 80 per cent, the use of iron and steel is not recommended, as the corrosion rate is excessive. (Spitz, A. W., Cast Iron and Steel, *Chem. Eng.*, Vol. 55, No. 5, p. 235, 1948.) On occasion, the dilution of high-concentration acid by absorption of moisture may take place and corrode cast iron or steel. Stagnant acid in pipe lines is a typical example which causes serious trouble.

Lead.—This metal satisfactorily resists cold acid of all strengths up to 95 per cent and hot acid of all strengths up to 80 per cent with temperatures up to 205°C. For some purposes antimonial lead is used in preference to chemical lead on account of its greater strength.

High-silicon Iron.—It has been successfully used for many years in applications involving sulphuric acid and solutions containing this acid. This alloy exhibits excellent resistance to all concentrations of the pure acid up to and including boiling temperatures.

It is available in the cast form only, and any required machining usually is done by grinding. A limitation of the high-silicon irons is their susceptibility to thermal or mechanical shock. However, if reasonable care is exercised, a long trouble-free life can be expected. A variety of engineered equipment is made with this material, such as pumps, valves, heat exchangers, heaters, jets, fans, ejectors, kettles, nozzles, tanks, pipes, and tower sections. (Luce, W. A., High Silicon Irons, *Chem. Eng.*, Vol. 55, No. 7, p. 227, 1948.)

Durimet 20.—Sulphuric acid and solutions containing this acid are successfully handled under many conditions of concentration and temperature by Durimet 20. This alloy shows negligible corrosion in all acid concentrations at 70°F. Although an increase in temperature indicates an increase in corrosion rate, highly satisfactory resistance is obtained at all concentrations up to temperatures slightly below 176°F. However, the resistance at 176°F. depends greatly upon the acid concentration. Satisfactory resistance is obtained at this temperature up to 65 per cent concentration. Acid in the 65 to 93 per cent range at 176°F. is particularly vicious in its attack on all stainless alloys, and although care is sometimes necessary in recommending Durimet 20 in this range, numerous successful applications are on record. Durimet 20 also shows an acceptable rate of corrosion for boiling acid up to 10 per cent.

This alloy is available in the form of castings and equipment made from castings such as pumps, valves, fans, ejectors, jets, and mixing nozzles. A limited number of wrought forms are now available.

Although the high-silicon iron can be recommended for all concentrations and temperatures of acid, it is sometimes limited in its scope when a high-strength machinable alloy is required or when contaminants such as sulphurous acid or hydrofluoric acid are present. It is for these services that Durimet 20 excels and is used in preference to the high-silicon iron. (Luce, W. A., Durimet, *Chem. Eng*, Vol. 55, No. 6, p. 223, 1948.)

Chlorimets.—Field tests conducted on Chlorimets 2 and 3 indicate that they can be applied successfully to most of the severe acid services encountered. As a general rule, Chlorimet 2 should be used under reducing conditions and Chlorimet 3 under oxidizing conditions. The 2 alloy is recommended in preference to the 3 alloy for acid strengths above 35 per cent at 176°F. and from 10 to 60 per cent at the various boiling temperatures. (Luce, W. A., Chlorimets, *Chem. Eng.*, Vol. 55, No. 8, p. 224, 1948.)

Glass-lined Steel.—Process equipment made of glass-lined steel has full resistance to H_2SO_4 at all concentrations at temperatures up to 500°F.

Hastelloys.—The Hastelloys have found numerous applications in chemical industry for service with sulphuric acid. For concentrations above 50 per cent, alloy A is recommended up to a maximum temperature of 160°F.

Alloy B will handle 60 per cent concentrations up to the boiling point; for concentrations above 60 per cent, alloy B is recommended up to a maximum temperature of 300°F. Neither alloy A nor B is recommended for mixed acids or for use when sulphuric acid is mixed with strong oxidizing agents, such as cupric sulphate or ferric sulphate.

Alloy C will handle 50 per cent concentrations up to the boiling point; for concentrations above 50 per cent, alloy C is recommended up to a maximum temperature of 150°F. This alloy will also handle mixed acids, such as nitric and sulphuric, as well as sulphuric acid containing oxidizing salts.

Alloy D was developed for handling sulphuric acid at all temperatures and concentrations. However, a word of caution is necessary in connection with the use of this alloy at 55 per cent concentration at boiling temperature. Alloy D has been subjected to these conditions for long periods of time. No appreciable attack will be evident for weeks; then suddenly a rapid rate of attack will develop. The cause of this phenomenon is not known as yet.

All four grades of Hastelloy are widely used for handling sulphuric acid. Alloys A, B, and C are used in the form of heating coils, blowpipes, steam legs, agitating equipment, pumps, valves, and piping; alloy D is used in the form of valves, piping, pumps, and bayonet tube heaters. (Chisholm, C. G., Hastelloy, *Chem. Eng.*, Vol. 55, No. 5, p. 238, 1948.)

Stainless Steels.—In solutions of pure sulphuric acid the useful range of stainless steels is limited. Types 316 and 317 possess the greatest corrosion resistance of the stainless steels to sulphuric acid. The former can be used in up to 5 per cent pure acid solutions at room temperature, while 317 is useful up to the same concentration at 150°F. Pure concentrated acid (66°Bé.) at room temperature is safely handled by any of the chromium-nickel stainless steels. The intermediate concentration ranges of pure acid solutions are severely corrosive to the stainless steels, but solutions of these same concentrations with other materials also present often can be safely handled by these stainless steels. None of these alloys are suitable for fuming sulphuric acid. (Renshaw, W. G., Stainless Steels, *Chem. Eng.*, Vol. 55, No. 5, p. 242, 1948.)

Worthite.—Actual service has proved that this complex stainless steel in form of pumps, valves, and specialties (companion flanges, hose nipples, bar stock, screw machine products, and welding electrodes) is satisfactory for sulphuric acid service within certain limitations.

At ambient temperatures, all strengths of acid can be handled satisfactorily. A 175°F. limitation is placed on the acid at the 45 per cent concentration range; for a 93 per cent solution, a limitation of 125°F. maximum; for 98 to 100 per cent, a 160°F. maximum limitation is imposed. (Collinsworth, E. T., Jr., Worthite, *Chem. Eng.*, Vol. 55, No. 5, p. 235, 1948.)

Rubber Linings.—Linings have been extensively used for handling limited concentrations of acid. It is possible to handle satisfactorily 50 per cent concentration at room temperature with soft or semihard rubber. Concentrations up to 70 per cent can be handled at 120°F. with neoprene or special hard-rubber compounds. Tests indicate that concentrations up to 70 per cent at 158°F. can be satisfactorily handled with butyl rubber. Concentrations up to 25 per cent can be handled at temperatures up to 200°F. with special hard-rubber compounds. (True, O. S., Rubber Linings, *Chem. Eng.*, Vol. 55, No. 5, p. 235, 1948.)

Carbon and Graphite.—The resistance of carbon, graphite, and impervious carbon and graphite to the corrosive action of all but the most highly oxidizing concentrations of sulphuric acid solutions has been established in numerous applications over a period of years. All forms of carbon are inert to highly ionized concentrations of sulphuric acid.

In general, the use of one particular form is settled by the properties of the materials, such as resistance to the specified concentration and temperature, weight, cost, strength, machinability, size, thermal conductivity, and imperviousness. All the materials are practically immune to thermal shock. Graphite and impervious graphite are useful when high thermal conductivity is desired, while carbon and impervious carbon are heat insulators. The impervious forms are used when a nonporous structure is required, while the basic carbon and graphite forms find application in the handling of gases at atmospheric pressure and of liquids under very low head or where slight seepage is not objectionable. Since impervious carbon and impervious graphite have essentially equal corrosion resistance, the machinability of the graphite-base stock determines the use of that form for most applications. Karbate materials are twice as strong as the base stocks.

Structural carbon can be used with all concentrations of acid from 0 to 96 per cent by weight. Use in the vapor phase is limited only by the presence of sulphur trioxide at the upper limits of concentration and temperature. Graphite does not exhibit the degree of resistance to the high acid concentrations shown by carbon. The use of carbon is, therefore, preferred for concentrations above 60 per cent by weight, and the structural carbon used in such concentrations should have a negligible content of the graphite form. In lower concentrations, the easily machined graphite is often preferable. Porous carbon and graphite exhibit corrosion-resistance properties similar to those of the basic forms. Carbon and graphite are inert in reducing conditions at all commercial temperatures; in atmospheres where oxidants are present, temperatures to the threshold air oxidation temperatures of 600 and 800°F. are suitable for carbon and graphite, respectively.

Karbate, impervious carbon, and graphite are suitable for concentrations of acid solutions from 0 to 96 per cent. Resistance of the carbon-base and graphite-base materials is identical for practical purposes. Processing temperatures to 340°F. are permissible with both impervious carbon and impervious graphite; in vapor-phase applications considerably higher gas-stream temperatures are possible when means for keeping the body temperatures of the material below 340°F. are provided. (Palmquist, W. W., Carbon, Graphite, *Chem. Eng.*, Vol. 55, No. 6, p. 226, 1948.)

Tantalum.—This metal can be used for concentrated acid at steam pressures up to 150 lb. It is recommended that tests be made when temperatures are expected to exceed 170°C., reported Schribner before Chicago Section of A.C.S., December, 1947. He stated that it should be remembered also that sulphate scale may be deposited upon heat-transfer surfaces which will reduce operating efficiency unless tantalum surfaces are cleaned frequently.

Monel.—This alloy will find its principal applications at concentrations of less than 80 per cent acid by weight, and in this range it will usually offer the best available combination of corrosion-resistance and good mechanical properties. In air-free acid, corrosion is extremely low at concentrations up to 80 per cent, and even in air-saturated acid below 80 per cent concentration at room temperature, maximum corrosion, at about 5 per cent concentration, is equivalent to less than 0.04-in. penetration per year.

The normal effect of increasing temperature is to accelerate corrosion. However, the lower solubility of dissolved oxygen at elevated temperatures may cause a decrease in corrosion rates above a critical temperature determined by the concentration of the acid, which in the case of 5 per cent acid is 176°F. When the concentration of oxidizing substances is low, increasing temperature, below the boiling point, will have little effect in acid under 60 per cent concentration. Corrosion rates in boiling solutions are likely to be somewhat erratic owing to complex effects associated with dissociation of the acid in contact with the metal. In such cases it is best to test the metal under exact conditions of use.

Phenolic Coatings.—Baked phenolic industrial coating will withstand dilute and up to 35 per cent concentrations of sulphuric acid solutions at any temperature up to and including boiling. For concentrations over 35 per cent, the maximum operating temperature is 150°F.

This type coating will withstand acid fumes up to a concentration of 250,000 ppm. at a maximum operating temperature of 80°F.

Silver.—Dilute sulphuric acid, *e.g.*, 10 per cent, does not attack silver even on boiling if air is excluded. An aerated solution of 10 per cent sulphuric acid corrodes silver slightly at room temperature, strongly on boiling (1.4 mils per year). Concentrated sulphuric acid dissolves silver at room temperature, very readily on boiling. (Rosenblatt, E. F., Precious Metals, *Chem. Eng.*, Vol. 55, No. 6, p. 223, 1948.)

Palladium.—Palladium is resistant to dilute and concentrated sulphuric acid at room temperature regardless of whether air has access or not. Boiling 10 per cent sulphuric acid attacks at the rate of 1 mil per year. At 150°C., concentrated sulphuric acid dissolved palladium fairly rapidly, especially if aerated. (*Ibid.*)

Gold.—Gold is extremely resistant to dilute and concentrated sulphuric acid, whether aerated or not. Even up to boiling temperatures the corrosion loss is negligible. Though gold is superior to any other unalloyed precious metal, some of the gold-platinum alloys are equally corrosion resistant and show superior mechanical properties which made them preferable for construction of equipment. (*Ibid.*)

Platinum and Platinum Alloys.—Platinum is completely resistant to dilute sulphuric acid under any conditions. It is attacked only very slightly by concentrated sulphuric acid even at high temperatures; for example, at 250°C. it shows a loss of only 0.07 mil per year; at 300°C., 0.7 mil per year. Even with this small attack, it is inferior to gold in resistance to this acid. The commercial platinum alloys with rhodium, iridium, and ruthenium show about the same corrosion properties as platinum alone but are preferable from the mechanical standpoint. Gold-platinum alloys, with a gold content of 70 per cent or more, are just as resistant as gold and are definitely superior mechanically. They are used in all cases where optimum corrosion resistance against sulphuric acid at high temperature is required; when other oxidizing agents are present, *e.g.*, in sulphuric acid containing some nitric acid, platinum and platinum alloys containing no gold are definitely superior to gold-platinum alloys.

Precious metals, especially platinum and its alloys, have found many applications in the sulphuric acid industry. A substantial proportion of sulphuric acid is made in the contact process using platinum metal catalysts. Platinum contact catalysts are often in use for 10 years or longer, and the loss over this time is more likely caused by dusting than by chemical attack. Large concentrators have been in use for many decades to concentrate sulphuric acid produced by the lead-chamber process. Platinum anodes are the preferred materials for inert anodes in many electrolytic baths containing sulphuric acid solution. They possess certain advantages even for nickel plating in special applications. Hydrogen peroxide is produced in cells using exclusively platinum anodes, as platinum is the only metal which will withstand the extremely corrosive conditions. Even platinum anodes show a small but continuous loss which in the case of platinum-clad anodes makes the use of a substantial thickness of the platinum cladding desirable. (*Ibid.*)

Haveg.—Maximum concentration of sulphuric acid for which Haveg is ordinarily recommended is 50 per cent, whether intended for a hot- or room-temperature application. This concentration, of course, refers to that in water solution, and it should be stressed that there is no sharp break in performance at this concentration. Such factors as temperature and the presence of other chemicals play an important role in stronger solutions, and it is therefore advisable to conduct tests under actual or simulated operating conditions where higher concentrations are involved.

Probably the most important field for Haveg involving sulphuric acid is in the metallurgical industry. It is extensively used in the form of cylindrical and rectangular tanks, fume systems, pumps, and piping for copper and steel pickling where acid concentrations of 5 to 20 per cent are commonly employed. Its scope in such applications is broadened by its excellent resistance to sulphuric pickling solutions containing other agents such as hydrochloric acid or ferric sulphate. Fabrication of this plastic material in inexpensive molds and an ingenious joint construction make feasible the production of long sectional troughs and rectangular tanks for use in the continuous pickling of wire and strips. (Mampe, E. P., Haveg, *Chem. Eng.*, Vol. 55, No. 7, p. 236, 1948.)

Illium.—It is usefully resistant to all concentrations of sulphuric acid at temperatures up to 60°C. under most conditions of aeration and agitation. It can be used with most concentrations except the most corrosive range of 65 to 80 per cent at temperatures up to 90°C. It is usefully resistant to boiling solutions of concentrations less than 50 per cent.

Illium has been found to be especially useful for parts of pumps and other equipment handling both chamber-process and contact-process acid, the complex sulphuric acid solutions used as rayon spinning baths, and the hot oxidizing solutions resulting from acid extraction of phosphates, alum, and other minerals.

Packaging

This acid can be shipped in glass bottles or boxed glass carboys (for acid of not over 100.5 per cent H_2SO_4). Metal barrels or drums are used for acid of 60°Bé. or acid of greater strength provided such acid has a corrosive effect on steel measured at 100°F. no greater than 66°Bé. commercial acid.

Lead-lined metal barrels or drums can be used for acid of not over 93.2 per cent H_2SO_4.

Rubber-lined metal barrels or drums can be used for acid of not over 42°Bé.

Tank cars, I.C.C. specification 103A or 103A-W, are used for acid of 1.5591 sp. gr. (52°Bé.) or greater strength.

Rubber-lined tank cars can be used for acid of not over 42°Bé.

SULPHURIC ACID—HYDROCHLORIC ACID

A tantalum coil has been in use for boiling a mixture of sulphuric and hydrochloric acids.

A Karbate centrifugal pump has been in service for 5 years handling a mixture of 7 per cent sulphuric acid and 30 per cent hydrochloric acid for the knock-down scrubbing of HCl gases from Mannheim furnaces.

SULPHURIC ACID—HYDROFLUORIC ACID

Although high-silicon iron is recommended for all concentrations and temperatures of sulphuric acid, it is sometimes limited in its scope when contaminated with hydrofluoric acid. It is for this service that Durimet 20 excels and is used in preference to high-silicon iron. Pumps of Durimet 20 are used by a chemical company to handle a solution containing 10 to 20 per cent sulphuric acid plus 1 to 5 per cent hydrofluoric acid at 120 to 140°F.

SULPHUROUS ACID—SULPHURIC ACID

Sulphurous acid, being of unstable composition, is very readily oxidized, in part, to sulphuric acid upon exposure to air. (Watkins, W. A., Durimets T and 20, *Chem. Eng.*, Vol. 54, No. 8, p. 209, 1947.) Although 18-8S and 18-8S Mo stainless steels are recognized as being satisfactory for pure H_2SO_3, the fact that some H_2SO_4 may be present makes it expedient to select an alloy such as Durimet T or Durimet 20. Both of these alloys possess excellent resistance to sulphurous acid of any concentration or temperature either with or without sulphuric acid contamination.

In the manufacture of sulphurous acid, the gases coming from the sulphur combustion chambers generally contain some SO_3. If the gases are passed through a spray-type washer and cooler, the SO_3 combines with water and the resultant weak sulphuric acid is disposed of. Many installations, however, permit the SO_3 to be carried on through the coolers and into the absorption towers. In either case the possible presence of sulphuric acid makes the selection of an alloy such as Durimet a wise one.

Although high-silicon iron is recommended for all concentrations and temperatures of sulphuric acid, it is limited in its scope when contaminated by sulphurous acid.

The Chlorimet alloys are not recommended for use with sulphurous acid.

Stainless steel Types 304, 308, 316, 317, and 329 have been widely used in the sulphite pulp industry. (Anon., Stainless Steel, *Chem. Eng.*, Vol. 54, No. 9, p. 214, 1947.) Of this group, Types 316 and 317 are preferred for heat exchangers, digester circulating systems, and relief lines which are exposed to the liquors containing sulphuric and sulphurous acids formed by the combination of sulphur dioxide and water.

Types 430 and 316 afford long service life in commercial equipment for handling combustion products containing SO_2. Corrosion in such applications is encountered chiefly in the presence of condensed moisture, which permits the formation of mixtures of sulphurous and sulphuric acids. Type 430 is used for parts of stacks and flues that are subject to operating temperatures above 300°F. where condensation does not occur. Type 316, which is more resistant to sulphurous acid and weak sulphuric acid, is used for the cooler sections of the equipment.

The higher alloyed nickel-chrome-moly alloys such as Worthite have proved more useful than Types 316 and 317 when some sulphuric acid is present. (Pratt, W. E., Worthite, *Chem. Eng.*, Vol. 54, No. 7, p. 221, 1947.) Worthite pumps have been widely used for pumping sulphurous acid where there is no question but what 18-8 moly alloys would have given excellent service. Worthite pumps, being a standardized alloy for Worthington chemical pumps, are available more quickly at a lower price, and repair parts are always available. This situation does not apply to castings, pipe fittings, and valves; hence Worthite in these forms is used only where very high temperatures or where the presence of sulphuric acid makes the Worthite more economical at the higher cost.

There is some indication that Worthite and similar alloys should be applied with caution in very hot mixtures of sulphuric and sulphurous acids where the oxidizing capacity of such solutions is reduced to nearly zero—especially in connection with systems involving large surfaces of lead. It is believed that this environment can cause "activation" of the alloy concurrently with "passivation" or involving of the lead surfaces by creating a heavy coating of lead sulphate. In a closed system it is possible that eventually the lead may become cathodic to the alloy, and with very large areas of cathodic lead being connected to an alloy pump or valve of small area, the anodic current density on the alloy part could cause severe galvanic corrosion.

One of the large sulphite pulp mills tested Worthite in a mixture of 5 per cent H_2SO_4 and 0.5 per cent H_2SO_3 at 176°F. No loss resulted. Subsequently this mill installed a Worthite pump for circulating 5 per cent H_2SO_4 at 180°F. over a scrubbing tower to remove SO_3 gas from the SO_2 gas. It was found that the H_2SO_3 built up to 5 per cent concentration. The scrubber and the connecting lines were lead and, of course, galvanically connected to the Worthite pump. After 6 months the rate of corrosion on the Worthite proved excessive. The surfaces were blackened and showed the characteristic appearance of galvanic corrosion. If the investigation now under way indicates this to be the main factor in the corrosion, simple insulation of a Worthite pump from the lead would permit its use. No such insulation of Worthite in somewhat similar environments (as mentioned above) has been necessary, but other installations may have allowed some oxidizing capacity of the circulated solution.

If any users of nickel-chrome alloys in H_2SO_4—H_2SO_3 solutions are experiencing unexplained corrosion of a piece of equipment in a lead system, it would be well to investigate the oxidizing capacity of the acid and to try insulating the alloy equipment from metallic contact with the lead.

TALL OIL

In the kraft-pulp process pine wood is treated with alkaline cooking liquors in digesters. During this step in the process the caustic saponifies the fats and resins in the pine wood. Later these saponified fats and resins along with the other liquor are removed from the pulp and sent to evaporators. In the evaporation of the black liquor there is a separation of the saponified fats and resins.

In recent years some kraft-pulp mills have made it a practice to treat the saponified fats and resins with sulphuric acid to separate the free fatty acids, which are known as "tall oil." These are mostly linolic, oleic, linolenic, and abietic acids. A few of the mills recover these acids; others ship the crude tall oil to refiners who make a specialty of the refining of these oils.

Production

Materials of Construction.—The refining operations demand special materials of construction, since fatty acids are distilled at temperatures approaching 700°C. In an investigation (Ward, L. E., Jr., and F. C. Vilbrandt, Corrosion Characteristics, in the Distillation of Fatty Acids, *Virginia Polytech. Inst., Eng. Expt. Sta. Series, Bull.* 30, 1937) the following conclusions were reached:

1. Copper, nickel, aluminum, and their alloys have corrosion rates and pitting and scaling characteristics too high to permit their use as materials of construction for fatty-acid stills.

2. Stainless steels up to and including 18-8 chromium-nickel content without molybdenum are unsatisfactory in their corrosion-resistant properties.

3. 18-8 chromium-nickel stainless steels with approximately 3 per cent molybdenum added are satisfactory in their resistance.

4. Molybdenum in chromium-nickel alloys allows reduction in the content of chromium-nickel for corrosion-resistant alloys.

5. Stainless steels with a minimum nickel content of 8 per cent and a minimum chromium content of 22 per cent are satisfactory, and increasing the chromium

content above the percentage increases the resistance of the alloy to corrosive attack by crude fatty acids. The choice of the particular alloy composition will depend on economic factors.

6. Silicon in chromium-nickel alloys shows no additive resistance toward fatty acid corrosion.

7. It is indicated that the resistance of the high-chromium stainless steels is due to the property of chromium of forming an oxide film over the surface of the alloy that is impervious to the action of crude fatty acids. The protective quality of this film is probably dependent upon the distance between the chromium atoms on the surface.

Corrosion tests conducted with Inconel against fatty acids (tall oil) under temperature conditions as encountered in the recovery of fatty acids in kraft mills have indicated that the corrosion rate for Inconel is as low as 0.002-in. penetration per year of continuous operation. Tubes of this metal of 2½ in. o.d. and 0.003-in. wall thickness are said to be in successful operation in a fatty-acid still. The entrainment separators of this still are also made of Inconel. (Anon., Monel, Nickel and Inconel in Pulp and Paper Mills, *International Nickel Co. Bull.* C-3, p. 20, 1938.) Inconel is also used for tall-oil heaters.

Results of corrosion tests conducted in crude tall oil and semirefined tall oil furnish evidence of the corrosion resistance of not only Inconel but also nickel and Monel. The results of these tests recommend Inconel or Inconel-clad steel for services such as crude-tall-oil storage, nickel-clad steel for storage of semirefined tall oil, and Monel for tall-oil pumps. Monel is being used for sulphuric acid splitting of black-liquor soaps to make tall oil.

Worthite equipment is in actual plant service for handling tall oil at 320°F. and also for the handling of a mixture of tall oil and sulphuric acid.

Durimet 20 pumps and valves and high-silicon iron plug valves are extensively used for handling a tall oil and sulphuric acid mixture at 200°F. The acid concentration is usually 5 to 10 per cent. Excellent service is being received after many years. The presence of the sulphuric acid makes this a difficult corrosion problem.

TANNIC ACID

Tannic acid, a glucoside of gallic acid, is very sensitive to certain metals. The principal requirement in considering materials of construction is that no iron or steel material be present owing to the formation of iron tannates, which even in minute quantities ruin the product from a color standpoint.

Copper and copper alloys in particular do not form dark-colored compounds with tannic acid. For this reason copper is used for such equipment as pressure extractors, vacuum evaporators, pipe, condensers, and autoclaves. The particular alloy to be used is determined largely by cost considerations. In the larger and heavier equipment such as pressure extractors or autoclaves, straight copper is used exclusively. The fittings for these vessels are made of brass. Vacuum evaporators are made of copper, bronze, or brass. Pumps and pipes for handling tannin extracts are generally either bronze or brass.

Other metals such as nickel, Monel, Durimet 20, and Worthite are suitable, also glass-lined steel.

Wood has been found to be satisfactory for construction of storage and processing tanks and tubs. (Anon., Tannic Acid, *Chem. & Met. Eng.*, Vol. 41, No. 10, p. 533, 1934.)

The industry had an abrasion problem that was solved by the use of Stellite on chippers and shredders.

TARTARIC ACID

There was a time when many corrosion problems plagued the tartaric acid industry, but fortunately most of them have been solved. At the present time, the equipment that is available if properly installed and fabricated of suitable materials is certain to last for many years.

Production

Materials of Construction.—Until fairly recently evaporator tubes gave difficulty, but this trouble has now been taken care of satisfactorily through the use of a perforated steel tube coated with lead. (Skidgell, F. M., Tartaric Acid, *Chem. & Met. Eng.*, Vol. 41, No. 10, p. 533, 1934.) Some concerns use lead-covered copper tubes, while hard lead is best for evaporator bodies. Lead-lined wood is suitable for the storage tanks of first-stage liquors. For the last-stage liquors aluminum and chemical stoneware make satisfactory storage tanks. Pumps of high-silicon iron, bronze, and stainless steel are used. Filter presses are constructed from wood. Dissolving tanks for the first-stage liquors are made of lead-lined wood and for the last-stage liquors aluminum. Screens are silk, brass, bronze, or Monel. Aluminum, 18-8 stainless steel, and Monel have all been used successfully for crystallizers.

From another source (Black, J. W., Manufacture of Tartaric Acid, *Ind. Chem.*, Vol. 14, pp. 443–444, 521–524, 1938; and Vol. 15, pp. 100–104, 1939) comes the information that evaporators are glass-lined iron pots, vats or generators are large wooden tanks with stirrers, filter presses are cast iron, filtering backs are wooden troughs lined with lead, granulating tubs consist of wooden vessels, lead-lined, with lead cooling coils, or the tubs are glass-lined iron pots. Stirrers have a lead-covered iron spindle and fork to hold the wooden agitator. The centrifuge is lead-lined steel with a copper cage or basket. Liquor from the black presses is evaporated in glass-lined iron pots in wooden steam chests. Stirrers are glass-covered. The dryer is a heated chamber provided with glass shelves. Grinding is done in stone mills.

Also, according to another source, it is known that considerable Haveg piping is used in tartaric acid manufacture, rubber-lined kettles and stainless-steel dryers are favored. Monel crystallizing tanks and supercentrifuges are used. Also, a Monel-lined rotary dryer is in use.

Tartaric acid has some action on aluminum, but processing in aluminum equipment introduces no compounds which are objectionable in the commercial applications of the product. These are the preparation of baking powder, tanning, photography, and textile finishing. On the other hand, the action of tartaric acid on lead and some other metals is objectionable because this acid is extensively used in food products and the products of corrosion would cause contamination.

Process.—Tartaric acid is obtained from wine lees, argols, tartars, and calcium tartrates. (*Ibid.*) In the first the acid is present mainly as potassium acid tartrate. It is necessary to convert this to calcium tartrate for further treatment.

The raw material is put into a wooden vat or generator with water and chalk to convert all the potassium acid tartrate into normal tartrate, and calcium tartrate is added. When the process is complete, calcium sulphate is added. This converts the potassium tartrate into calcium tartrate. All tartaric acid has now been converted to calcium tartrate, and the mixture is pumped to a cast-iron filter press in which the calcium tartrate is retained and the potassium sulphate is filtered off. The calcium tartrate is washed and then knocked out into the decomposing vat. Here it is treated with sulphuric acid, which converts it to tartaric acid and calcium sulphate.

The tartaric acid is filtered from the calcium sulphate in lead-lined backs through a cloth of jute or hessian supported on a perforated wooden board. The filtrate and washings are conveyed to evaporators and concentrated. Weaker liquors from the backs are not directly evaporated but are used for other purposes.

The evaporated strong liquor from the backs is run down to vats fitted with lead cooling coils and agitated until the crystals have separated. This crystallized liquor is centrifuged, and the crystals washed. The liquors are sent back to the steamers for further recovery or sent to purification in the case of old liquors.

Crystals are subjected to further purification. In a wooden vat are placed partially purified crystals, water, animal charcoal, and barium sulphide. The whole mass is agitated cold, and the mixture brought to a definite gravity. Afterward it is filtered through presses, and the solution of tartaric acid passes to the final evaporators.

Evaporation is carried out in glass-lined iron pots in a steam chest, where the solution is concentrated to the crystallization point. It is then cooled. The salts are again crystallized, washed, dried, and ground to requisite fineness.

Handling

In the absence of air tin is not oxidized by 5 per cent tartaric acid, but in the presence of air oxidation of the metal takes place at the surface of the solution, oxides of tin and stannous tartrate being formed. (Hamlin, M. L., and F. M. Turner, "Chemical Resistance of Engineering Materials," Reinhold Publishing Corporation, New York, 1923.) Tenth normal and hundredth normal solutions of tartaric acid attack the tin coating of cans rapidly in the air but scarcely at all in vacuum or in an atmosphere of carbon dioxide.

Packaging

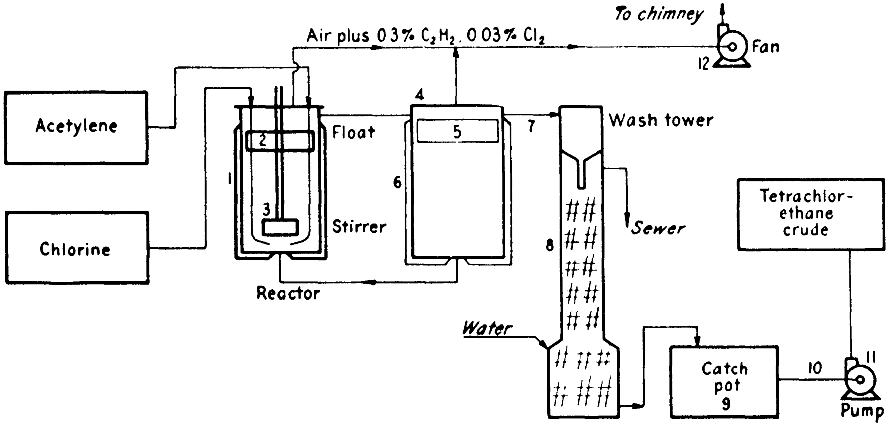
Shipping containers for tartaric acid are wooden barrels or boxes.

TETRACHLORETHANE

At the Alexander Wacker A.G. plant in Burghausen there are two methods for making tetrachlorethane by the reaction of acetylene with chlorine. (Carpenter, G. B., Chlorinated Hydrocarbons from Acetylene, FIAT Final Report 843, Technical Industrial Intelligence Division, U.S. Department of Commerce.)

Production

Materials of Construction.—The first process is operated at atmospheric pressure in stirred lead-lined tanks and is known as the "old process." Fume pipes are lead, and the exhaust fan of stoneware. The wash tower is made of Haveg packed with ceramic raschig rings.



Tetrachlorethane (old process).

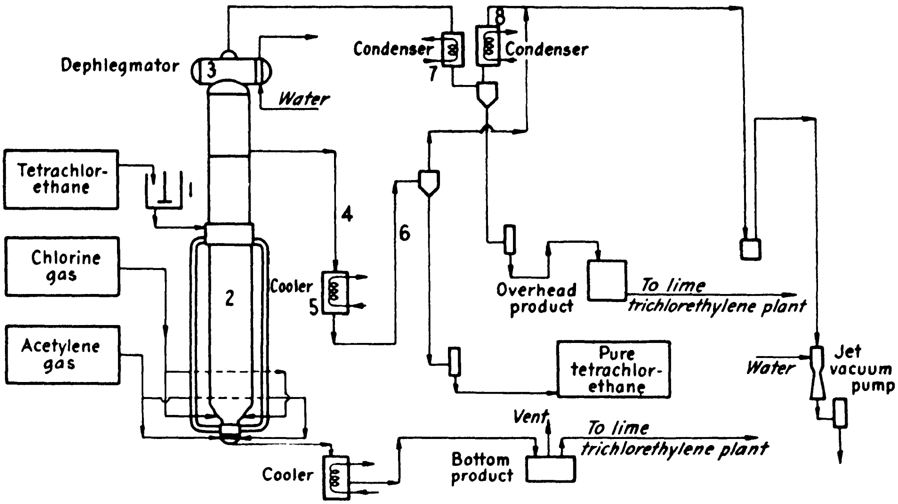
1. Lead-lined steel
2. Monel
3. Lead-lined
4. Wood
5. Monel
6. Lead-lined steel
7. Lead
8. Haveg with porcelain rings
9. Lead-lined
10. Lead
11. Chemical stoneware
12. Chemical stoneware

In the second method, the reaction is carried out in a homogeneous lead-lined tower. This is known as the "new process" or "tower system" and is considered by Wacker to be much superior to the older method. The dephlegmator is lead-lined. (*Ibid.*)

In the United States it is reported (Ford, C. E., *Chem. Eng.*, Vol. 54, No. 2, p. 134, 1947) that Karbate has been used with tetrachlorethane. It is said to be resistant to this chemical at all concentrations up to 100 per cent at boiling. Another source reports that several nickel-clad-steel chlorinating vessels are used for acetylene at a large plant in the United States.

Old Wacker Process.—Acetylene is fed into a lead-lined steel tank. Chlorine is introduced to the tank through a separate line. The acetylene and chlorine lines are steel, and that portion of the lines inside the tank is lined, on the outside only, with lead. There are iron check and slide valves in the acetylene lines and conical valves for regulation of the chlorine.

The tank is charged with tetrachlorethane containing ferric chloride. On top of the liquid in the tank is floated a Monel cover 300 mm. from the top of the tank. The purpose of this floating top is to reduce evaporation loss of tetrachlorethane. A tank of the same size, but without gas inlets and without stirrer, is connected in a parallel position with the first tank, one line connecting the bottom of each tank and one line connecting about 300 mm. below the top of each tank. An exhaust fan draws a stream of air from just above the Monel floats in each tank. The fume pipes are lead, and the exhaust fan of stoneware.



Tetrachlorethane (new or tower system).

1. Lead-lined
2. Homogeneous lead-lined with stoneware rings
3. Lead-lined
4. Lead-lined
5. Lead
6. Lead
7. Iron
8. Lead

The exhaust air from the fan contains acetylene and chlorine. It also contains tetrachlorethane to the amount of about 1 per cent of that manufactured. Temperature in the tanks is maintained at 70 to 80°C. Initial heating of the charge to 60°C. is accomplished by a small lead coil.

The unstirred tank is equipped with an overflow where the tetrachlorethane product is sent to a water washer for removal of dissolved ferric chloride. The water wash tower is of Haveg packed with ceramic rings. The product, a crude tetrachlorethane, is handled in lead pipe lines and by chemical-stoneware pumps.

New Wacker Process or Tower System.—For the new process, the reactor is a homogeneous lead-lined steel tower. The bottom is filled with stoneware rings. On top of the packed tower is a tubular, lead-lined dephlegmator which is water-cooled. Before starting, the reactor is charged with tetrachlorethane. At a point near the bottom of the tower, acetylene gas enters through two tangential gas inlets. Chlorine gas is fed into the tower by similar inlets.

A small amount of gas leaves the top of the dephlegmator and passes through a condenser to a water jet vacuum pump. This gas contains HCl amounting to 1 per cent of the chlorine fed. From the condenser before the vacuum pump is obtained liquid containing 90 per cent tetrachlorethane and 10 per cent dichlorethylene. From the side of the reaction tower, 2 m. below the dephlegmator, liquid tetrachlorethane is removed, cooled, and sent to product storage.

TITANIUM DIOXIDE

Titanium dioxide is used in making a white pigment of which there are two types, anatase titanium dioxide and rutile titanium dioxide. The hiding power of the latter type is greater. Although the titanium dioxide and the pigments are not corrosive, the process of manufacture involves the handling of extremely corrosive materials and complete elimination of contamination from the equipment.

Production

Materials of Construction.—Inasmuch as sulphuric acid is one of the principal raw materials in the process, much of the equipment is lead-lined steel, wood, or concrete. Some brick-lined concrete and steel equipment is used. The final vacuum filter and the continuous dryer are stainless steel, since sulphuric acid is no longer present.

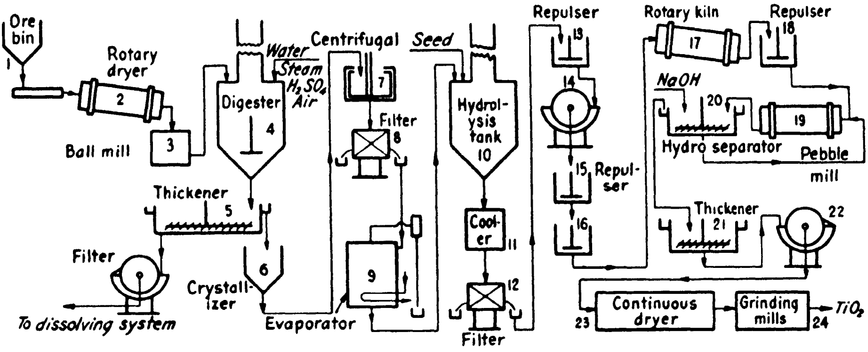
Old and new plants use a large number of high-silicon iron and Durichlor pumps and valves to handle the acid-process liquors and slurries. These same materials and Durimet 20 are used in the latter stages of the process. Wrought Carpenter 20 is also used.

Anatase Process.—The ore, ilmenite, is dried in a rotary dryer and ground in a steel ball mill. The ground ore is then digested with sulphuric acid in order to dissolve out the titanium dioxide. A large concrete or steel tank lined first with lead and next with acid brick is used for this purpose. Antimony trisulphite and steam are added to the ore and acid. The result is titanium and other sulphates. Water is added after the reaction is complete to dissolve the titanium sulphate from the mass that was formed.

The digester load goes to a lead-lined thickener from which the clarified liquor is decanted off, and the mud is pumped out from the bottom of the tank. Part of the copperas is crystallized out of the decanted liquor in a vacuum crystallizer. The crystals are washed in a centrifuge to recover adhering titanium solution. This solution goes to a second clarification to remove any residue that remains. It is treated with diatomaceous-earth filter aid and passed through a filter. This filter has a vinyl resin filter cloth. The dilute solution is evaporated.

In hydrolysis the soluble titanyl sulphate is converted to an insoluble dehydrated titanium compound, metatitanic acid. When anatase hydrolysis is being carried out, boiling up to 6 hr. is required, but for rutile pigment half that time is all that is necessary. The seed that is added is the starting point for condensation of the pigment from solution.

From the lead-lined hydrolysis tank the precipitated pigment goes to a cooling tank of the same materials of construction. The cooled material is filtered through a lead-lined wood filter with paper pulp precoat, which removes the iron sulphate and other soluble salts. The insoluble metatitanic acid is further purified by repulping the filter cake reducing ferric iron present with titanous sulphate and then washing.



Titanium dioxide (anatase).

1. Concrete, wood, steel
2. Steel
3. Steel, manganese balls
4. Lead and brick-lined concrete
5. Lead-lined steel or concrete
6. Lead-lined steel
7. Lead-lined steel
8. Lead-lined steel, vinyl resin filter cloth
9. Lead-lined steel
10. Lead and brick-lined concrete with lead coils
11. Lead-lined steel with lead coils
12. Lead-lined wood with pulp precoat
13. Lead-lined steel
14. Stainless steel
15. Lead-lined steel
16. Lead-lined steel
17. Brick-lined
18. Steel
19. Steel
20. Lead-lined concrete
21. Lead-lined concrete
22. Stainless steel
23. Stainless steel
24. Steel

The cleaned filter cake is treated with a conditioning agent and passed through a rotary calciner or kiln at 950°C.

The pigment on leaving the kiln is treated according to the use for which it is to be put. If it is to be wet milled, the dry material is ground and quenched in water. The slurry is treated with caustic soda and sent to a hydroseparator. The coarse material returns to the pebble mill, while the finer material goes to the thickener. Here it is coagulated by the addition of calcium chloride and goes to the bottom. It is then removed and goes to a stainless-steel vacuum filter.

The partially dried cake is further dried in a stainless-steel continuous dryer. Dried pigment is ground in a steel mill and sent to storage.

TITANIUM TETRACHLORIDE

Production

Materials of Construction.—Ordinary mild-steel plate and pipe are not corroded by either crude commercial or purified titanium tetrachloride. Corrosion does occur, however, where the tetrachloride is exposed to the atmosphere, and hydrolysis can occur such as at discharge pipes and valves. Such corrosion is due to the hydrochloric acid formed by the hydrolysis reaction and usually is minimized by capping open pipe ends when not in use. Stainless steels of the 18-8, 18-8 Mo, and straight chromium types behave the same as mild steel and are preferred for flowmeters and valves that are occasionally removed from a closed circuit for cleaning. This is done best by generously flushing with water; hence, the rust resistance of the stainless alloys is an advantage. Hastelloy C can be used where atmospheric corrosion cannot be avoided. Brass valves, brass inserts in pipe unions, and brass-trimmed valves cannot be used because the usual brass alloys are corroded rapidly by titanium tetrachloride.

Rubber packing and gaskets must be avoided, as rubber is rapidly attacked by the tetrachlorides. Lead gaskets are satisfactory in pipe flanges. Valve stems, flowmeters, sight gage glasses, and similar equipment are best packed with asbestos. Lubrication of valve stems is difficult, as the usual petroleum and graphite products form addition compounds with titanium tetrachloride and become inoperable quickly. Silicone lubricant gives good service wherever contamination is unimportant, because silicones are slowly soluble in liquid titanium tetrachloride. Outside screw and yoke valves are preferable to the inside-screw type, and it is convenient to have interchangeable bonnets so that a valve stem in need of repacking can be exchanged for a previously repacked bonnet. (Stoddard, C. Kerley, and Emil Pietz, Pilot Plant Distillation and Purification of Titanium Tetrachloride, *U.S. Dept. Interior, Bur. Mines Rept. Invest.* 4153.)

TOILET PREPARATIONS

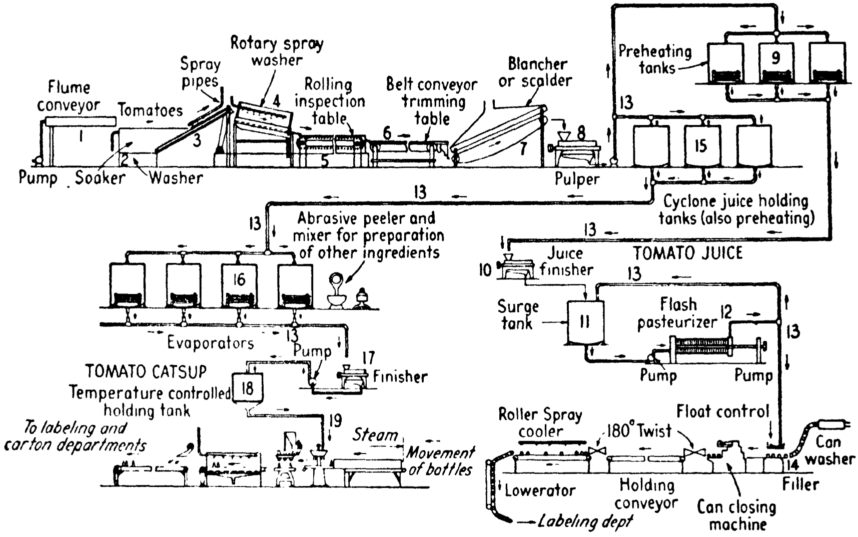
Mixers made from or lined with Monel are used in many soap plants for the mixing of soap washing compounds, shaving soaps, toilet waters, cosmetics, etc. Such mixers are usually fitted with Monel agitators where portable mixers are used, Monel is employed for the shafts and propellers. Kneading agitators made from Monel are employed in the manufacture of tooth paste. (*Chem. Age,* p. 307, Oct. 6, 1934.)

Centrifugal extractors fitted with Monel-metal baskets are employed in the production of various washing compounds, bath salts, etc. Both Monel and pure nickel are employed for components of filling machines handling toilet creams, liquid soaps, shampoos, and tooth pastes. (*Ibid.*)

Glass-lined steel is employed extensively for the mixing and storage of these products, especially since dissolved metals and resultant turbidity or discolorations must be avoided.

TOMATO JUICE

Like other tomato products, the juice contains corrosive acids, citric and malic, which give trouble unless special materials of construction are used for equipment.



Catsup and tomato juice (schematic diagram).

1. Steel
2. Steel
3. Steel
4. Steel
5. Steel
6. Steel
7. Steel
8. Stainless steel
9. Stainless steel, glass-lined, wood
10. Stainless steel
11. Stainless steel, glass-lined
12. Stainless steel
13. Glass, stainless steel
14. Stainless steel
15. Stainless steel
16. Stainless steel, glass-lined
17. Stainless steel
18. Glass-lined, stainless steel
19. Stainless steel

Production

Materials of Construction.—In the tomato-products plant there are batteries of jacketed stainless-steel cooking kettles with portable mixers. Tomato juice is delivered hot from holding tanks to finishers, which remove the last traces of shreds, discharging into stainless-steel tanks from which the juice is pumped to holding tanks supplying flash pasteurizers. Juice flash pasteurizers are equipped with stainless-steel feed and delivery lines, etc.

Glass-lined steel tomato cookers with stainless-steel or copper coils are also used. In some plants glass-lined tomato-juice tanks with conical bottoms receive juice from the finishers and act as balance tanks before the initial concentration in glass-lined vacuum pans. Glass-lined storage tanks are also used.

Glass piping is now in use in a few plants for handling tomato juice.

Extensive use is made of high-silicon iron and Durimet 20 in the production of tomato juice and catchup. The high-silicon iron pumps, valves, and piping have proved entirely satisfactory after several years of continuous service.

TOMATO PASTE

Tomatoes contain a highly corrosive acid which calls for special materials of construction.

Production

Materials of Construction.—Glass-lined steel is used for evaporators, storage tanks, and other equipment and is said to be very efficient and generally satisfactory. Stainless steel is also used successfully for evaporators and other pieces of equipment. Steam-jacketed nickel kettles are used for evaporation of tomato juice in making the paste in some plants.

Process.—In the Atwater, Calif., plant of the Capolino Packing Corp. tomatoes are dumped into high-pressure washers. (*Glass Lining*, Pfaudler Co., Vol. 15, No. 3, p. 15, 1945.) They are elevated from washers to inspection belts and discharged into a scalder and crusher. Pulp is then pumped through vacuum tubular preheaters to cyclone pulpers, and the pulp passes through finishers to storage tanks and is kept at 185°F.

Actual concentration of this tomato pulp into paste takes place in stainless-steel calandria-type evaporators.

When the desired concentration has been reached, the tomato paste is piped to glass-lined, steam-jacketed, and totally enclosed tanks equipped with stainless-steel agitators and automatic steam controls. From these storage tanks the product is pumped through vacuum preheaters to bring the temperature to 195°F. and fed to filling equipment.

In the Turlock Cooperative Growers plant at Modesto, Calif., the finisher juice in the paste plant is stored in glass-lined conical bottom tanks. (Simpson, J. E., Turlock Cooperative Growers Tomato Paste, *Glass Lining*, Pfaudler Co., Vol. 15, No. 2, p. 12, 1944.) The juice is then drawn into a glass-lined evaporator. The type of evaporator installed here is a glass-lined steel calandria unit. From the evaporator, finished paste is drawn into a jacketed, closed, glass-lined balance tank.

TOMATO PRODUCTS

Materials of Construction.—Glass-lined steel, stainless steel, wood, copper and its alloys, and other materials must be used in the processing and handling of tomatoes and tomato products to prevent corrosion caused by the citric and malic acids present.

Copper.—Tomato-canning equipment has chrome plate, copper, brass, or bronze wherever the machinery may come in contact with the product. Such parts include a rotary pump made of bronze casting. This pump conveys the product from one point to another, usually through copper or brass pipe. The machine which crushes and strains the product is made almost entirely of brass and bronze or another copper alloy. (Cole, C. S., Copper, Brass and Bronze, *Food Ind.*, Vol. 7, No. 12, pp. 583–584, 1935.)

Stainless Steel.—At one time it was considered difficult to can tomatoes successfully, *i.e.*, without impairing the flavor and vitamin content, but stainless steel proved to have no chemical reaction. Stainless-steel equipment employed by the canning industry includes kettles, pans, pulping equipment, transfer lines, and filling machines. In the tomato-products plant there are batteries of jacketed stainless-steel cooking kettles with portable mixers.

Glass-lined Steel.—In making tomato paste glass-lined vacuum pans are said to be very efficient. These same vacuum pans are also used in preparing tomato purée, which differs mainly in degree of concentration. Some plants use an open glass-lined cooker with a single heater coil for concentrating tomato pulp to purée. In making catchup a glass-lined deaerating unit is used by some engineers.

Glass.—Indoor and outdoor tomato-pulp transportation lines of glass piping are in use. A catchup cooking kitchen uses such a glass pipe line for hot tomato products.

Monel.—Tomatoes are being dried in slices and packed in that form for stewing. The tomatoes are washed, steamed, or dipped in boiling water to loosen the skins, chilled in cold water, peeled and cored by hand, sliced, spread one layer deep on trays, and dehydrated at not above 150°F. to less than 5 per cent moisture. Monel screen or other screen not attacked by acid should be used.

Other Materials.—For brine processing and storage redwood tanks have had extensive use. (California Redwood Association, *Tech. Bull.* 16–5.) Vacuum tomato-cooking pans with the inside surface nickel-plated 0.010 in. thick have been used successfully.

Process.—Tomatoes are dumped in a flume conveyor, which provides a first wash and transportation to the soaking tanks from which the tomatoes are lifted to a rotary or squirrel-cage washer. Tomatoes are discharged from the washer onto a traveling roller conveyor which revolves tomatoes for inspection. They are discharged to a second sorting table.

Passing inspection, the tomatoes enter steamers, which loosen the skins, discharging into crushers which wash the fruit. From these machines the crushed tomatoes enter the stainless-steel pulpers. Here the skin and seeds are separated from the juice and pulp. Juice is pumped through stainless-steel or glass pipe to the kitchen, and the seeds, skins, and cores go to the seed department for recovery and processing of the seeds.

In the kitchen the juice is heated and held in wooden or glass-lined tanks for further processing to tomato juice or evaporated to make tomato pulp or, with the addition of spices and flavoring, to make bean sauce or catchup.

TRICHLORETHYLENE

Production of trichlorethylene at the Burghausen plant of the Alexander Wacker A.G. was investigated by an American engineer after the war. (Carpenter, G. B., Chlorinated Hydrocarbons from Acetylene, FIAT Final Report 843, Technical Industrial Intelligence Division, U.S. Department of Commerce, 1947.)

Production

Materials of Construction.—For the most part trichlorethylene production equipment can be made of ordinary cast iron and steel. Some lead and lead-lined steel are used for handling the crude tetrachlorethane. The Germans used both enamel-lined steel and ordinary cast iron for storage tanks for the product.

Process (Reaction of Tetrachlorethane with Lime).—In the Burghausen plant of Wacker trichlorethylene was made by two methods. In one case it was produced from tetrachlorethane made by the "old process" by reacting with lime water at a temperature of 88°C. in a cast-iron tower reactor. (*Ibid.*)

Crude tetrachlorethane is mixed with lime slurry and added to the middle of the cast-iron column. Live steam is introduced at the bottom. The top section of the tower is packed with raschig rings. On top of the packed section there is a dephlegmator. A reflux is maintained, and the product from the top of the dephlegmator is the constant-boiling mixture of trichlorethylene and water. This mixture is condensed, and the water layer discarded to the sewer.

The crude product is first topped in an iron column to remove low boilers. This is mainly dichlorethylene. The feed to the iron heads column is just above the bottom section. Bottoms are fed directly to the middle of a column containing 45 bubble-cap plates. Pure trichlorethylene is condensed overhead and sent to an enamel-lined storage tank.

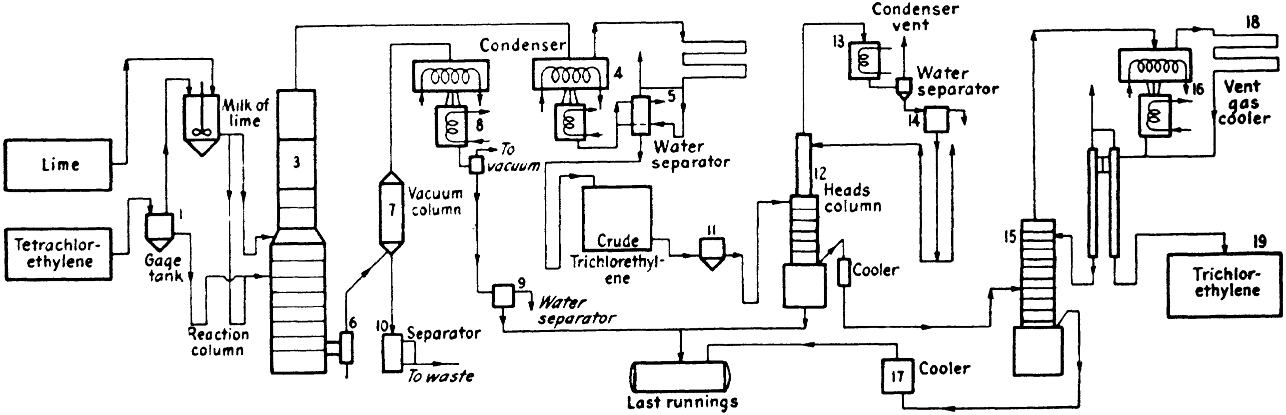
Process (Vapor-phase Cracking of Tetrachlorethane).—Tetrachlorethane is fed to a lead-lined evaporator and after preheating in an iron vessel is fed to the iron converter and then to a degassing column.

The feed of tetrachlorethane passes through the vaporizer, leaving at 150°C. This evaporator contains lead-covered steel coils. The feed goes to a tubular iron exchanger, where it is preheated. No corrosion is experienced where the vapor tetrachlorethane is handled.

The iron converter contains a rectangular box through which are run steel tubes. The catalyst is charged outside the tubes. High-pressure steam is circulated inside the tubes. The catalyst is 30 per cent barium chloride on activated carbon.

No corrosion difficulties have been experienced in the reactor if the temperature was kept below 300°C. Corrosion is shown by the appearance of too much hydrogen in the hydrogen chloride product.

Gases from the converter are fed to the middle of a raschig-ring-packed iron column. The dephlegmator on top of the column cools the HCl gas to 50°C. It

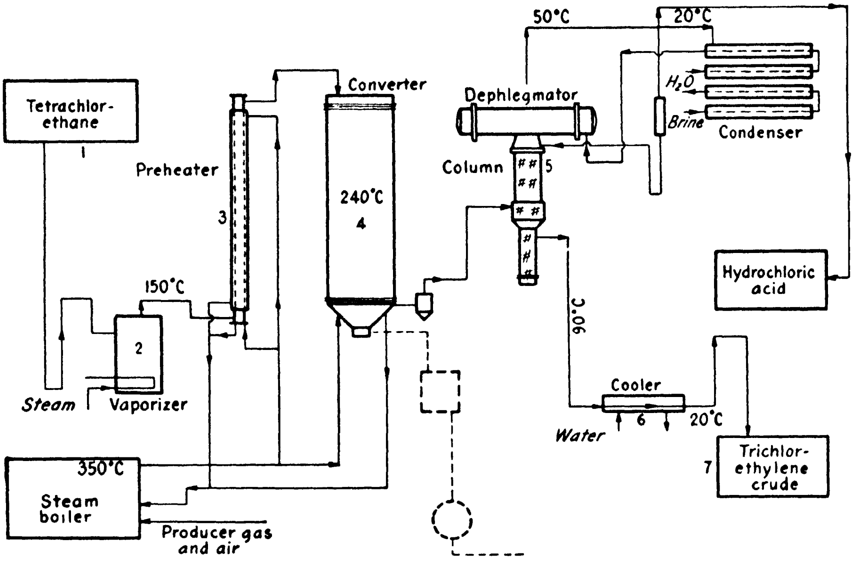


Trichlorethylene (by reaction of tetra with lime).

1. Lead-lined iron
2. Iron
3. Cast iron
4. Iron
5. Lead-lined iron
6. Iron
7. Iron
8. Iron
9. Lead-lined iron
10. Iron
11. Lead-lined iron
12. Cast iron
13. Iron
14. Lead-lined iron
15. Cast iron
16. Iron
17. Iron
18. Iron
19. Enamel-lined steel

is then further cooled by a condenser to 20°C., and the liquid separated is returned to the top of the column.

At the bottom of the degassing column the liquid is heated to 90°C. It then passes to the cooler, where it is cooled to 20°C. and sent to enamel-lined storage tanks.



Trichlorethylene.

1. Enamel-lined steel
2. Lead-lined steel
3. Iron
4. Iron with steel tubes
5. Iron
6. Iron
7. Enamel-lined steel

Handling

Trichlorethylene can be handled if dry by plain iron or steel. It does not ordinarily affect aluminum. A certain amount of attack may occur, however, in the presence of water and at elevated temperatures. (Brown, H., *et al.*, "Aluminum and Its Applications," p. 292, Pitman Publishing Corp., New York.) Durimet 20 is resistant at all concentrations and temperatures. Worthite is in use handling this chemical. Karbate is resistant to all concentrations up to 100 per cent at boiling. The Germans were using enamel-lined steel for storage tanks.

Under normal conditions, trichlorethylene can be stored satisfactorily in galvanized-iron, black-iron, or steel equipment. (Manufacturing Chemists Association, "Trichloroethylene," Chemical Safety Data Sheet SD-14.)

When free from water and at atmospheric temperature, chlorinated hydrocarbon solvents are not corrosive and steel equipment ordinarily can be used to handle them. However, in the presence of entrained water or a water layer and, particularly, at elevated temperatures, such as are encountered in the distillation and recovery of the solvents, there is appreciable hydrolysis with resulting formation of dilute hydrochloric acid. (International Nickel Co., Resistance of Nickel, Monel and Other High-Nickel Alloys to Corrosion by Hydrochloric Acid, Hydrogen Chloride and Chlorine, *Tech. Bull.* T-29, 1945.) The development of acidity is accelerated by light and air. Under such conditions, steel frequently is rapidly attacked. Over a period of many years' service Monel and nickel have shown resistance to corrosion under these conditions. Both materials are used for distillation and recovery equipment in the manufacture and application of the solvents. Nickel-clad steel is used for degreasing tanks, also for stills and condensers in recovery of trichlorethylene in the solvent systems.

TRIISOPROPYLBENZYL CHLORIDE

The German I.G. Farben. at its Uerdingen plant produced triisopropylbenzyl chloride. (Adams, D. A. W., and W. Baird, Some Miscellaneous Chemical Intermediates and Products, PB 80401, Office of Technical Services, U.S. Department of Commerce.)

Triisopropylbenzene, paraform, and zinc chloride are charged to a glass-lined kettle. The mixture is stirred and heated to 75°C., and hydrochloric acid (anhydrous) passed in during 16 hr. at such a rate that a little HCl always passes out through the condenser. This rate is rapid at first but slows down during the reactions.

The aqueous layer is separated off, and the batch washed first with dilute sodium carbonate (10 per cent) then with water. To prevent emulsification the washing is done at 40°C.

The batch is now transferred to an oil-heated lead-lined still and distilled at 5 mm. Unreacted material comes over first, and the main product is collected at 110 to 145°C. per 5 mm. It should crystallize in the receiver.

TRINITROTOLUOL

It has been reported that during the recent war the Germans at Schlelausch were operating a continuous process for making trinitrotoluol.

Production

Materials of Construction.—TNT was made in cast-iron equipment. However, purification was carried out in stainless steel.

Process.—The process of nitration was carried out continuously in five nitrators and four separators arranged on an incline to permit of gravity flow from vessel to vessel. All vessels were fabricated in cast iron and were lagged with glass wool. The separators were fitted with glass inspection windows to show the interface between acid and nitrobody. The outlet from the nitrators was located about 1 ft. from the top of the vessel and consisted of lead pipe of 1½ in. diameter. From the bottom of each separator a pipe line ran to acid tanks on a lower floor, and a similar outlet from the liquid level in the separator ran to each succeeding nitrator.

Purification of the TNT by washing and sulphiting was also done by a continuous process, the plant consisting of four washers and four separators. As in the nitration plant the vessels were arranged on an incline to permit of gravity flow. The vessels appeared to be fabricated of stainless steel and lagged with glass wool.

The first washer was used for removing acidity by water washing, the second washer was used for the sulphite treatment, and the remaining two washers were again water-washing ones.

UREA

The commercial production of urea from carbon dioxide and ammonia is carried out in a continuous process.

Production

Materials of Construction.—As the synthesis is carried out at elevated temperatures and at pressures from 150 to 300 atm., it is necessary to construct the autoclaves to withstand these pressures. (Groggins, P. H., "Unit Processes in Organic Synthesis," 3d ed., p. 413, McGraw-Hill Book Company, Inc., New York, 1947.) Steel pumps of the hydraulic type are used successfully to pump liquid ammonia and liquid carbon dioxide separately into the autoclaves. The liquid in the autoclaves, consisting of a mixture of urea, water, ammonium carbonate, and free ammonia, is, however, highly corrosive to ordinary materials of construction at elevated temperatures. (Thompson, Krase, and Clark, *Ind. Eng. Chem.*, Vol. 22, p. 735, 1930.) Ordinary iron and steel are quickly dissolved in it, and chromium steel and many other alloys are rapidly attacked.

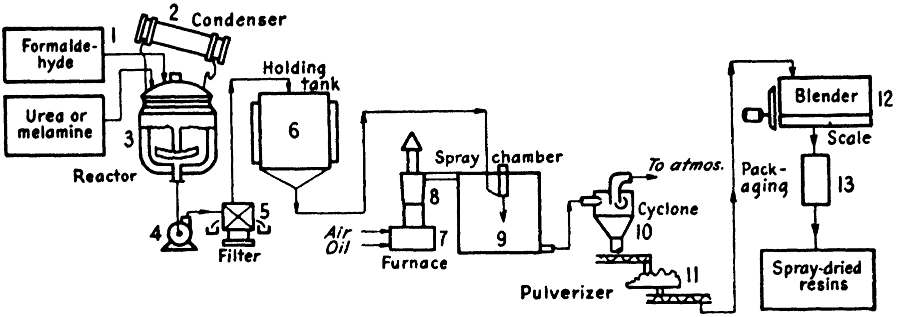
Lead and silver are two of the most resistant materials, and these metals are employed as linings for the autoclave and stills used in the process. Resistant steel alloys are used in construction of the parts where lower temperatures are encountered.

Process.—About 102 parts of ammonia and 44 parts of carbon dioxide are compressed and delivered separately as liquids (or compressed gases) into a steam-heated autoclave at 190°C. maintaining an internal autoclave pressure of 200 atm. (Groggins, *loc. cit.*) About 2 hr. is required for the passage of the materials through the autoclave, during which interval the reactants are almost wholly converted to ammonium carbonate, which, in turn, is converted largely to urea.

From the autoclave, the melt, consisting of 11.7 parts of ammonium carbonate, 51 parts of urea, 68 parts of ammonia, and 15.3 parts of water, is cooled to approximately 150°C. and is then admitted to a urea still, which is maintained at 60°C. Here 42.3 parts of unconverted ammonia and any unreacted carbon dioxide are removed and collected for return to the system. The urea-water solution is then delivered to a crystallizer maintained at 15°C., where 18 parts of the remaining free ammonia are removed by a suitable suction pump compressor. The resultant magma is passed to a continuous centrifuge whereby 30 parts of crystalline urea are obtained. The mother liquor can be variously used in the manufacture of mixed fertilizer.

UREA-FORMALDEHYDE RESIN

This resin was among the first such materials to be made and used in this country. To prevent corrosion of processing equipment or contamination and discoloration of product, special materials of construction are used.



Urea or melamine-formaldehyde resin.

1. Concrete lined with phenolic resins, stainless steel
2. 18-8 stainless steel, Karbate
3. 18-8 stainless steel
4. Steel
5. Cast iron

6–12. Steel

13. Fiber drums

Production

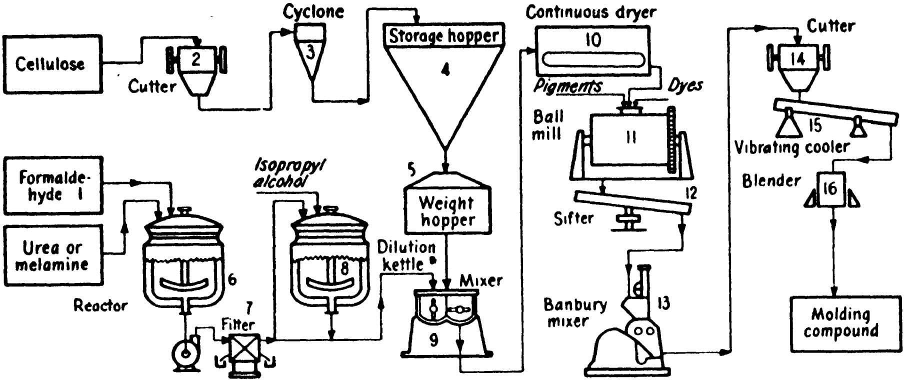
Materials of Construction.—Urea-formaldehyde reaction kettles are made of Type 347 stainless steel or aluminum.

According to corrosion tests made by the International Nickel Co. nickel, Monel, and Inconel or steel clad with these materials are satisfactorily resistant to corrosion in the manufacturing process. Nickel-clad steel is used for resin storage tanks.

Process.—Urea and formaldehyde, the raw materials, are fed separately by conveyors into a unit that combines the functions of weighing machine, mixer, and reaction vessel. (Bakelite Opens New Automatic Phenolic Moulding Powder Unit, *Inter. Ind.*, p. 422, 1948.) When they are brought together, there is a rapid fall in temperature, which is made good by heating the chamber to bring it back to room temperature. A catalyst is added to start the reaction.

The resin is run off from the reaction vessel to a cooling chamber below, where the temperature is lowered to halt the reaction.

Cellulose pulp, plasticizers, lubricants, and hardening agents are added in a heated vacuum mixer, emerging in the form of a coarse white powder. This is fed on to the hot rolls from which it emerges as a thin sheet which is fed to a crusher.



Urea-formaldehyde molding compound.

1. Concrete lined with phenolic resin, 18-8 stainless steel, rubber-lined steel, aluminum
2. Steel
3. Steel
4. Galvanized iron
5. Steel
6. 18-8 stainless steel, aluminum
7. Steel, cast iron
8. 18-8 stainless steel, aluminum
9. 18-8 stainless steel
10. Galvanized iron
11. 18-8 stainless steel
12. Steel
13. 18-8 stainless steel
14. Steel
15. Steel

VANILLA EXTRACT

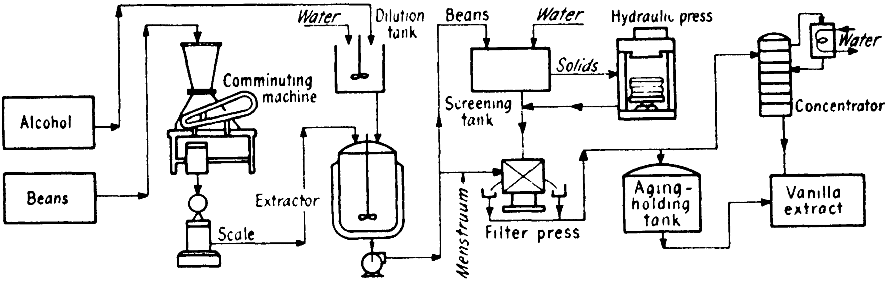
The chemical substance from which vanillin (the principal flavoring constituent of vanilla) is formed occurs in the ripening uncured fruit in the form of a glucoside called "glucovanillin." (Anon., Vanilla Has an Interesting History, *Food Ind.*, Vol. 20, No. 12, p. 1774, 1948.)

Production

Materials of Construction.—For many years wood was standard for construction of equipment and is still used in some plants. However, the new plants have gone to stainless steel. Both of these materials are used to avoid iron pickup, which causes turbidity. The essential pieces of equipment in the modern extraction plant for vanilla of the Standard Vanilla Co., Los Angeles, are stainless steel. The other equipment is ordinary steel. In some plants glass-lined steel is in general use for percolators and for storage of the finished extract.

Process.—The first step in the actual processing of vanilla in this California plant is the shredding of the whole beans. (Breidenback, R. W., Vanilla Extract Processing Speeded, *Food Ind.*, Vol. 20, No. 12, pp. 1772–1774, 1948.) This is done in a delicately balanced comminuting machine without raising the temperature of the vanilla. The beans are shredded into particles of small enough size to permit thorough penetration of the solvent and efficient solution of the bean extractive matters. The shredded vanilla is weighed very carefully to the requirements of the batch formula and is then ready for extraction.

In the extraction process, dilute ethyl alcohol is used almost universally as the solvent, and to the trade, the extracting solvent preparation is known as the "menstruum." To obtain the best results, the menstruum should contain approximately 50 per cent ethyl alcohol. Before coming into contact with the vanilla, the menstruum is always mixed thoroughly. It will extract nearly all the vanillin, volatile oil, water-soluble constituents, and most of the color and resins—though it will not extract the undesirable gum, fat, and wax.



Vanilla extract. Older plants depend on wood for equipment, while the newer plants are stainless steel throughout.

In order to take out the vanilla, the shredded fruit is placed in the menstruum in an extractor. This, basically, is a specially designed, stainless-steel-jacketed tank in which the vanilla and menstruum are continually agitated with a churning motion for a period of 24 hr. and at a slightly increased temperature. This agitation assures the contact of all the finely divided vanilla particles with the warm menstruum and allows an extraction as complete as it is possible to get with the initial menstruum. When this is accomplished, the menstruum is drawn off from the solids into a stainless-steel holding tank. A second menstruum is pumped in with the "beans" and is handled in the same manner.

After separating the second menstruum from the solids, the beans are pumped from the extractor into a screening tank, where they are washed twice with water. They are then pressed in pads in a hydraulic press, under approximately 300 tons of pressure, in order to remove the alcohol.

All the extracts and wash water are combined and filtered—through either a plate-and-frame filter or a horizontal-plate-type filter with the aid of diatomaceous earth—into stainless-steel storage tanks. Here, the batch is tested, built to the proper alcohol content and volume, and then allowed to age for a minimum of 3 weeks.

From the aging tanks, the finished extract is pumped, when ordered, to a bottling machine for packaging in gallon jugs or into barrels for shipment to the customer.

VARNISH

Materials of Construction.—For many years copper was the most commonly used material of construction in the varnish industry. More recently stainless steel, Monel, Inconel, aluminum, and nickel are displacing copper for the fabrication of linseed-oil boiling kettles and varnish kettles.

In some modern varnish plants stainless steel is used throughout the kettle installation to prevent corrosion by fatty acids and other corrosive substances formed when the varnish materials are heated. While comparatively little is known of the complex reactions which occur in the varnish-cooking process, it is well established that the quality and especially the color of the final product are improved by the use of stainless-steel equipment. This includes the kettle, thermocouple, heat exchanger, and the various valves, pipe fittings, etc.

Copper is used in varnish making principally because it is necessary to adopt every precaution to prevent overheating, and this needs the employment of a metal which has high heat conductivity. (Wright, A. G., Copper and Copper Alloys: Some Aspects in Applications in Plant, *Chem. Age*, p. 438, June 10, 1939.) In many instances where the body of the kettle is made of some other metal, the base is copper or a copper alloy.

Copper kettles generally consist of a cylindrical body with a welded or riveted base made much thinner than the sides so as to withstand the direct fire which is the normal method of heating. (Copper Development Association, "Copper in Chemical Plant," pp. 64–65, London, 1936.)

The natural hard resins such as copal and amber must be heated in order to render them soluble in some solvent medium before they can be utilized for varnish manufacture. The heat necessary for this is high enough to dry-distil a portion of the resin, and the operation is therefore frequently carried out in small copper stills with condenser attached. After heating is completed, the cooled resin is dissolved in the solvent and filtered, copper being the supporting metal for the filter medium.

Kettles for production of varnishes and resins are frequently made of aluminum in order to take advantage of the high heat conductivity of aluminum equipment. The product is neither discolored nor contaminated by contact with aluminum. The aluminum alloy best suited to this class of service is 52S because of its good mechanical properties at the high temperature encountered in the processing of varnishes and resins. For the storage and piping of oils and solvents, aluminum tubing and tanks are frequently used. (Aluminum Co. of America, "Aluminum in Chemical Industry," p. 9, 1944.)

Monel kettles and other equipment are also used to ensure production of a light-colored varnish. Aluminum bronze is used for bottoms of varnish kettles, as it is particularly effective against oxidation at high temperatures.

VEGETABLES

In the dehydration of vegetables the trays used to carry the vegetables through the tunnel dryer have frames of pine, the bottoms are screens. For nonacid vegetables, galvanized screen has been used, but Monel screens are preferred, since they are more resistant to corrosion. For acid vegetables such as rhubarb and tomatoes, it is important that the Monel or wood slat trays be employed. The disadvantage of Monel is the fact that it cannot be used for blanching the vegetables in steam. If used for tomatoes, the slats of the wooden trays should be coated generously with confectioner's slab oil (an edible mineral oil) in order to minimize sticking of the dried products.

Rubber canning conveyor belts are made of a white cover to promote cleanliness and to facilitate efficient sorting. They are constructed so as to be easily cleaned with soap and water, are waterproof and impervious to the action of vegetables.

In canning vegetables brine is often added to the cans. Copper, brass, and bronze are useful in equipment for protection against corrosion by this brine. (Cole, C. S., Copper, Brass and Bronze, *Food Ind.*, Vol. 7, No. 12, pp. 583–584, 1935.) But in the case of certain products like sweet corn, which is subject to discoloration by very minute traces of copper, it is the best practice to tin the copper, brass, or bronze surfaces coming into contact with the corn. Tomato juice and canned tomatoes contain a highly corrosive acid, and again these metals are used for protection wherever the product comes into contact with the machinery. For example, bronze pump parts are used to handle tomatoes or tomato juice. Equipment for crushing and straining tomatoes is made entirely of brass, bronze, and another copper alloy. It is, of course, important that the equipment be thoroughly clean and bright before using it in contact with foods—a precaution that is important for any material of construction.

Even vegetables with peculiar characteristics or flavors that require special handling care have been satisfactorily processed in stainless-steel equipment.

One canning plant has several thousand feet of glass pipe for conveying those vegetables readily contaminated.

VEGETABLE OILS

Production of vegetable oils consists in considerably more than the unit operations of extraction, distillation, evaporation, drying, etc. (Gross, W. H., Modern Practice in Solvent Extraction, *Chem. & Met. Eng.*, Vol. 41, No. 4, pp. 80–84, 1941.) The individual operations must in many cases be carried out in such a manner that the products meet the exacting specifications of the food industries, and this requires rigid adherence to the practices with which only those having long experience in the fat and oil trade can claim thorough familiarity. For example, the operations must be carried out in equipment fabricated only from those materials which experience has shown to be free from any tendencies toward contaminating the oil with traces of certain metals. The presence of minute amounts of copper, as well as numerous other metals, is fatal to the stability of refined soybean oil. In edible-oil production, the corrosion problems incident to the choice of a solvent and materials of construction revolve, not around damage to the equipment, but rather around the damage caused by metallic contamination of the product.

Production

Two methods are used for obtaining vegetable oils and fats: (1) expression and (2) solvent extraction. The former method is the more often used in the United States.

Materials of Construction.—As far as vegetable oils are concerned, all principal pieces of equipment are fabricated from plain carbon steel. It may be pointed out that with regard to pipe fittings, valves, and pump parts, the use of copper or alloys containing copper is avoided. These metals have a detrimental effect with respect to oil quality. In the case of processes involving the production of food products by means of water extraction, stainless steel is used.

Solvent Extraction Process.—Typical of a modern solvent extraction plant is that of the Delta Products Co. in Wilson, Ark. While it is operating on cottonseed oil, the unit processes, sequence of operations, and general arrangement of equipment are typical of any solvent extraction plant no matter what the oil-bearing seed may be. (Tray, S. E., and C. W. Bilbe, Solvent Extraction of Vegetable Oils, *Chem. Eng.*, Vol. 54, No. 5, pp. 139–141, 153, 160–163, 1947.)

The first job is to break down the cellulose structure of the seed so that the solvent has access to the oil it must remove. This includes cracking, steaming, and flaking. The prepared meats are carried by belt conveyor to the top of the extractor, where they descend by gravity through an upward current of a solvent. Solvent overflows the top of the extractor, carrying the oil and lint of solids with it. This mixture of oil and solvent, called "miscella," is clarified first in a centrifuge and then in a plate-and-frame filter. From now on the operation is devoted to removing and recovering the solvent—from both the meal and miscella. The meal is elevated above the solvent level, squeezed fairly dry, and the final traces of solvent driven off in dryers. The solvent vapors are scrubbed with hot water to remove meal fines, then condensed.

Getting the solvent out of the miscella is not so simple. From the filtrate tank it goes through two preheaters to raise its temperature almost to the boiling point of the solvent, then into a long-tube high-velocity evaporator. The evaporator discharges into a flash chamber, where most of the solvent vapors pass off overhead to a condenser. The small amount of solvent that still remains in the oil is pulled out in a vacuum stripping column. The oil flows down from tray to tray against a rising stream of live steam, which is drawn off overhead and condensed with the solvent. The solvent and water mixtures from the condensers are separated in a continuous decanter. Oil from the bottom of the stripping column is now free of solvent and is ready for storage.

Milling Processes.—The first step is to clean the seed thoroughly, regardless of whether hydraulic presses or expellers are to be used. (Jamieson, G. S., "Vegetable Fats and Oils," 2d ed., pp. 200–210, Reinhold Publishing Corporation, New York, 1943.) The cleaned seed are fed, in the case of cottonseed, into delinters. When whole seed are to be pressed, the next step is to crush, heat, and press in hydraulic presses, or in the case of expeller mills, the seed are crushed in a disk grinder and dried in rotary hot air or grain dryers so as first to reduce the moisture content to 1 per cent before pressing in the expeller.

In the United States hydraulic mills press only decosticated seed. The separated meats are cooked from 215 to 220°F. and then pressed. The press is a steel box frame consisting of a series of horizontal steel plates. Above the top frame a heavy iron plate is fastened to the hydraulic piston cylinder by four vertical steel columns, which serve as guides for the sliding frames or boxes.

The usual practice is to allow the crude oil to run from the press into settling tanks. When the tank is filled, the oil is allowed to stand until the press foots have settled. At this stage, the clarified oil is drawn off into a clean storage tank. Some mills pass the oil through a filter press.

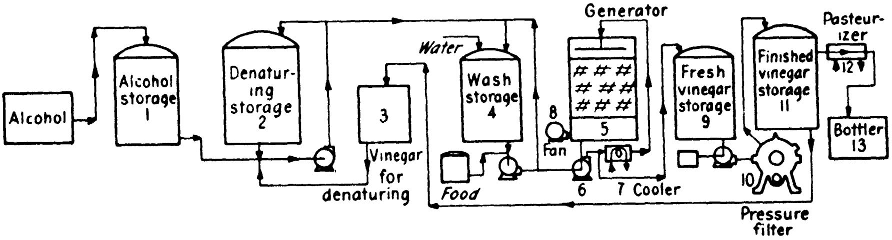
To produce an edible oil, the crude oil is refined by the caustic soda process, bleached, and deodorized.

VINEGAR

The acetic acid content of vinegar causes it to corrode some metals. The acid content in some cases is as high as 15 per cent. It is therefore necessary to use special materials for its manufacture and handling.

Production

Materials of Construction.—Wooden storage tanks have been used for alcohol, but it deteriorates wood, and modern usage trends to stainless construction.



Vinegar.

1. Stainless steel, wood
2. Wood
3. Wood
4. Wood
5. Wood with spargers of wood, stainless steel, or Durimet
6. High-silicon iron, Durimet
7. Stainless steel
8. Steel
9. Wood
10. Stainless steel
11. Wood
12. Type 316 stainless steel, high-silicon iron
13. Stainless steel

Piping: Wood, hard rubber, high-silicon iron, glass, stainless steel, Saran-lined steel

Valves: Wood, high-silicon iron

The pump, pipe, and fittings for pure alcohol need not be anything other than steel, although here again present trend is toward stainless.

For the pump, pipe, and fittings used to denature the alcohol, a corrosion-resisting alloy is required. High-silicon iron mixing nozzles are used in some plants to get quick mixtures easily. The vinegar denaturing tank may be wood. The wash storage tank is generally wood, but all pipe fittings and pumps must be corrosion-resisting alloys from the feed valve on.

The generator is a covered wood tank. It is equipped with stainless-steel gage glass valves to indicate the height of liquid in the well space. The tank outlet, piping, valves, pump cooler, sparger, and meter must be corrosion resisting. The air piping should be stainless, as this pipe runs into the generator where contact with the vinegar is made.

The packing is beechwood shavings, corn cobs, pecan shells, coke (iron free), or pumice, any material which will give surface and not deteriorate while wet.

Intermittent spargers are sometimes tee-shaped wood troughs. Continuous spargers may have spray heads of Durimet cast bodies with multiple stainless disks for the umbrellalike spray. The rotary-type spargers must be made of stainless, with a high-silicon iron pivot bearing.

A centrifugal pump is generally of high-silicon iron or Durimet. It is used to unload the generator.

Some plants use stainless double-pipe coolers which serve not only to cool the vinegar but also to convey it from the pump up to the sparger at the top of the generator.

For accurate control of the process, flowmeters and thermometers are required. A visible-float-type meter to measure vinegar and air is most satisfactory, the float being of Type 316 stainless steel as well as the wetted fittings. All thermometer bulbs in the vinegar should be of Type 316 stainless steel.

No corrosion problem is present with the air blower, but the piping is often stainless for appearance. Where it enters the generator, it must have a short piece of stainless-steel pipe.

All parts of the filter in contact with the liquid must be stainless. If the vinegar is in the form of pickle brine (with salt added), it is essential that low-carbon material be used and that welding technique be good.

The pasteurizer is a heat exchanger made of Type 316 stainless steel or high-silicon iron.

Often garlic, sweet basil, tarragon, and other flavors are added to vinegar. Salt and sugar are added to pickle brines. The mixers are generally of relatively small size, and the process is batchwise; hence wood tanks with stainless fittings and mixing blades are required. The bottling apparatus must be of stainless parts.

In all plants wood was originally used for piping. This was later supplemented by hard rubber or high-silicon iron. In some later plants Pyrex-glass and stainless-steel tubing are used. In one or two instances Saran pipe has been installed. High-silicon iron requires more supports than hard rubber or Saran. Stainless steel is more costly, and Saran age-hardens.

Pipe fittings are best in high-silicon iron because of cost, but if used with stainless tubing, the tubing must be flanged, which adds to the tubing investment.

High-silicon iron or Durimet valves are most widely used, although many very small plants have used wooden plug cocks.

Process.—Modern vinegar manufacture in this country is carried out in generators of the Frings, Ash, Owens, Lowy, etc., types. Alcohol is kept in storage tanks. It is denatured by mixing it with vinegar in sufficient volume to give about 10 per cent vinegar in the alcohol.

In the wash tank the alcohol-vinegar mixture is diluted with water to give a mixture of 12 per cent. Also food for the bacteria is added—generally brewer's malt. This is all thoroughly mixed by pumping in circulation. A generator is charged with 3.5 to 4 gal. of wash per cubic foot of packing. There is, in addition, a residual in the generator of vinegar of about an equal amount. The wash is recirculated over the generator through the sparger or spray head, and as the temperature rises owing to the bacterial action, water is admitted to the cooler or heat exchanger to control to the optimum temperature. Air is supplied to provide oxygen for oxidation of the alcohol to acetic acid.

When the conversion progresses, the alcohol is reduced to about 0.25 per cent, the acid increased to 10.5 per cent, and the batch is ready to be taken off. Depending on the efficiency of conversion, this takes a period of 10 to 30 days. The average modern plant gets a batch off in 15 days.

The vinegar is placed in intermediate storage. Most plants filter the entire output through a diatomaceous earth. White or distilled vinegar is often passed through a carbon filtration and polishing filter. This is especially required if the product is to be sold in clear glass.

Bottled vinegar must be pasteurized before bottling to prevent spoilage in the bottle.

Handling

High-silicon Iron.—Pumps, valves, pipe, and fittings of this material are used for handling vinegar and mixtures containing vinegar in the food industries. There are records of installations that have been in service for more than 20 years where the equipment is still in excellent condition. Equipment in service for 15 to 20 years handling strong vinegar containing about 10 per cent acetic acid shows no evidence of corrosion. (Staley, W. D., High-Silicon Iron, *Chem. Eng.*, Vol. 53, No. 12, p. 210, 1946.)

Durimet 20.—Valves, fittings, and hose connections and gage glass fittings of this alloy are giving satisfactory service with strong vinegar at normal temperatures.

Glass-lined Steel.—Vinegar is held in large glass-lined steel storage tanks.

Stainless Steel.—Type 304 stainless steel is highly satisfactory for almost every process involving vinegar, except some in which the presence of sodium chloride causes corrosive attack by pitting.

Wood.—Storage tanks of wood are used for storage of vinegar.

Rubber.—Lined piping and rubber hose are in use for conveying vinegar and cider.

Monel.—Filter cloth of Monel is used in filtering.

Saran.—Steel pipe lined with Saran is in use.

Bronze.—This metal can be used for pumps and other equipment in the handling of vinegar.

Packaging

Many plants do not make vinegar but purchase it from others. This requires transportation by tank truck or railway car. The tanks for conveying may be of wood, rubber-lined steel, or stainless-steel construction.

The vinegar as sold to the housewife is in glass bottles.

VINEGAR-SODIUM CHLORIDE

High-silicon iron pumps, valves, pipe, and fittings are used on strong vinegar mixed with brine (sodium chloride) such as is used in preparing pickles and olives.

Type 304 stainless steel is satisfactory for handling vinegar except in some cases where the presence of NaCl causes corrosive attack by pitting. This pitting effect is often completely resisted by Type 316, which can be used for certain kinds of preserving solutions containing vinegar, sugar, and NaCl.

VINYL ACETATE

Vinyl acetate monomer is produced in greatest volume in Germany at Hoechst a/Main, near Frankfurt. This installation is one of the most modern of the units which comprise the huge Hoechst group of plants of the I.G. Farben. chemical empire. (Greene, L. W., Vinyl Acetate, *Chem. Eng.*, Vol. 54, No. 7, pp. 98–99, 1947.)

Production

Materials of Construction.—Major items of equipment and metals used in their construction are as follows: Vaporizer, heat exchanger, separator, preheater, heater, catalyzer, and blower are made of ordinary steel; condensers, mist remover, and still are made of stainless steel (Fe; Cr, 18; Ni, 8; Mo, 3). In the first plant, aluminum was used instead of stainless steel, but the maximum life of equipment did not exceed 18 months.

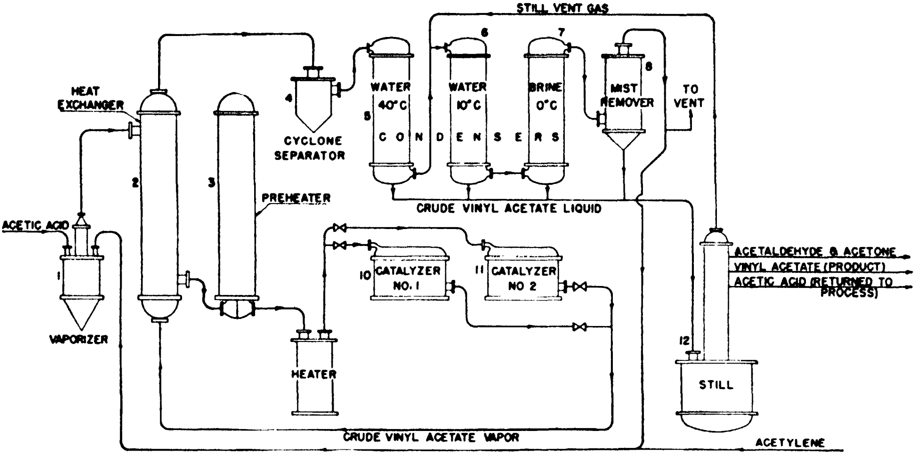
Process.—The catalyst consists of activated charcoal impregnated with a solution of zinc acetate. Dried catalyst in the form of granules contains 15 parts of metallic zinc to 100 parts of charcoal.

Calcium carbide is used for generation of acetylene in conventional wet-type units. Because it is essential in vinyl acetate manufacture to remove all traces of hydrogen sulphide and phosphine from the acetylene, the gas first is scrubbed with sulphuric acid of 80 per cent strength, followed by passage over a mixture of potassium dichromate and kieselguhr distributed in layers 2 in. deep on trays.

Purified acetylene, mixed with acetylene recycled from the process, is bubbled through acetic acid heated to 60°C. The rate of flow is adjusted so that the gas leaving the vaporizer carries with it about 23 per cent by weight of acetic acid. The gas travels through a heat exchanger, where it picks up heat from the vapor leaving the converter. It flows to a preheater (steam) and then into a high-pressure steam heater, where the temperature of the acetylene-acetic acid mixture is raised to 170°C. From the heater, the gas flows into the catalyzer.

When the catalyst is fresh, the gas temperature is held at 170°C., but as the life cycle of the catalyst approaches completion, the temperature is raised slowly to 210°C.

The crude vinyl acetate vapor emerging from the catalyzer passes through the heat exchanger and then to a separator, where carbon dust is removed. From this unit, the vapor enters a series of three condensers, the first of which is cooled with water at 40°C., the second with cold water at 10°C., and the third with brine at 0°C. Condensate from each of these three units, plus the liquid from the entrainment separator or mist remover, collects in a common line which flows to the still.



Vinyl acetate.

1. Steel
2. Steel
3. Steel
4. Steel
5. 18 Cr, 8 Ni, 3 Mo stainless steel
6. 18 Cr, 8 Ni, 3 Mo stainless steel
7. 18 Cr, 8 Ni, 3 Mo stainless steel
8. 18 Cr, 8 Ni, 3 Mo stainless steel
9. Steel
10. Steel
11. Steel
12. 18 Cr, 8 Ni, 3 Mo stainless steel

This condensate, which may be termed crude vinyl acetate, averages 60 per cent pure vinyl acetate and 40 per cent acetic acid. Actually three columns are used in the plant, and the distillation process is continuous. The low-boiling fraction is mainly a mixture of acetaldehyde and acetone, next is the vinyl acetate monomer, and finally acetic acid is recovered for return to process.

Resin formation during the distilling process is prevented by the addition of thiodiphenylamine to the crude vinyl acetate in the still. Because of this, it was found that the addition of stabilizer to the product in storage was unnecessary.

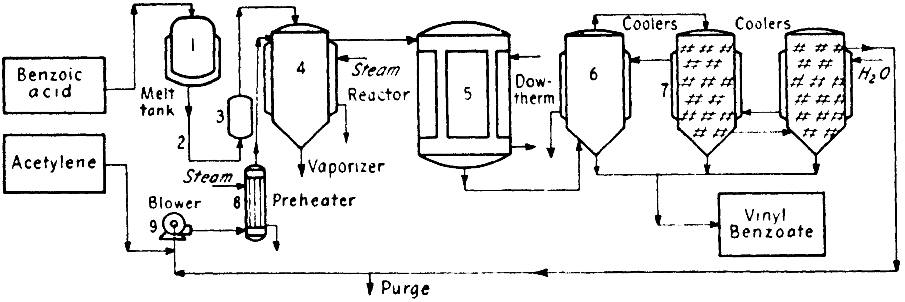
The yield of vinyl acetate varies from 92 to 95 per cent based on acetylene and 97 to 99 per cent based on acetic acid.

VINYL BENZOATE

When the American engineers visited Germany after the Second World War they found that the I.G. Farbenindustrie was producing vinyl benzoate on a semicommercial scale. (Carpenter, G. B., Production of Higher Vinyl Esters at Ludwigshafen, FIAT Final Report 935, Technical Industrial Intelligence Division, U.S. Department of Commerce, 1946.)

Production

Materials of Construction.—All equipment is of steel except the benzoic acid charge tank, lines and rotameter, and vaporizer, which are made of aluminum.



Vinyl benzoate.

1–4. Aluminum 5–9. Steel

Process.—Molten benzoic acid is fed from an aluminum gravity tank to an aluminum flash vaporizer, where it is vaporized into a stream of preheated acetylene. The mixture at 180°C. is fed to a steel tubular reactor heated by Dowtherm. The reactor contains 55 steel tubes charged with catalyst. (It is prepared from 8.75 parts of aluminum sulphate, 11.15 parts of cadmium nitrate, 5.7 parts of sodium hydroxide, and 74.5 parts of pumice.) The reaction temperature is 250 to 320°C., depending on the age of the catalyst. Exit gas is cooled in a series of five water-jacketed towers, the first of which is empty and the remainder packed with raschig rings. Unreacted acetylene is returned to the suction of a blower. Purge gas is vented to maintain 90 per cent acetylene in the system, and make-up acetylene is fed to hold 40 mm. Hg pressure on the suction of the blower. The discharge pressure of the blower is 80 to 200 mm., depending on the age of the catalyst. The acetylene cycle is 100 cu. m. per hr., and the benzoic acid feed is 30 kg. per hr. Acetylene make-up is 6.2 cu. m. per hr.

VINYL CHLORIDE

The vinyl chloride plant of the I.G. Farben. at Schkopau was visited in May, 1945, and was found ready to operate. [Boundy, R. H., and R. L. Hasche, Manufacturing of Thermoplastics in Plants of I.G. Farben., Combined Intelligence Objectives Committee, G-2 Division, SHAEF (Rear) APO 413, U.S. Department of Commerce.]

Production

Materials of Construction.—In the United States the production of vinyl resins made from acetylene employs stainless steels to make the process practical, and its use as reactors for esterification and other phases of the process is well established.

At the German plant much of the equipment was made of iron. The reactor was constructed entirely of iron. The vinyl chloride was stored in iron tanks.

Process.—Incoming acetylene at the Schkopau plant in Germany was dried with potassium hydroxide, and the hydrochloric acid with concentrated sulphuric acid. The iron catalyst reaction vessel contained 100 to 150 tubes. The catalyst was mercuric chloride on activated carbon. The operating temperature with fresh catalyst was 120°C. The reaction was at atmospheric pressure. Excess hydrochloric acid was removed with water, and the vinyl chloride cooled and condensed by a spray of 25 per cent calcium chloride solution at −40°C.

Distillation was carried out in ring-packed columns. The first still took vinyl chloride plus acetylene over the top and residual high-boiling chlorinated compounds from the bottom. The second removed acetylene overhead and pure vinyl chloride from the bottom. The vinyl chloride was stored in iron tanks underground. No inhibitor was added.

Packaging

Vinyl chloride can be shipped in ordinary steel tank cars.

VINYL ESTER OF TALL-OIL ACID

At Ludwigshafen the I.G. Farben. is reported to have been using a semicontinuous process for making vinyl ester of tall-oil acid.

To the tall-oil acid is added zinc oxide in a heated mixing kettle and heated for 2 hr. at 150°C. to remove water. This charge is cooled and pumped to a steam-heated steel tower. A steam coil is provided for heating, and a second coil for cooling. The reactor is purged with nitrogen, heated to 180°C., and an acetylene cycle started. Temperature is held before 200°C. Gas circulation is continued until 95 to 100 per cent of the calculated amount of acetylene has been consumed. The product is used without further treatment.

The reactor is steel and tends to protect itself by depositing a coating of solid polymer on the walls. It was stated that V_2A would probably be a better construction material. (Carpenter, G. B., Production of Higher Vinyl Esters at Ludwigshafen, FIAT Final Report 935, Technical Industrial Intelligence Division, U.S. Department of Commerce, 1946.)

VITAMIN D CONCENTRATE

Production of Vitamin D concentrate by the Wisconsin Alumni Research Foundation consists of an emulsion of Vitamin D_2 (irradiated ergosterol) in butter oil emulsified in milk solids which is canned and sterilized. The vitamin concentrate Dyne, consisting of D_3 (irradiated cholesterol) emulsified in milk solids, is also carried out by the Foundation.

Production

Materials of Construction.—The processing line in which the products are handled is stainless steel throughout. (Anon., Packaged Sunshine, *Glass Lining,* Vol. 17, No. 3, pp. 11–12, 1948.)

Process.—The process consists essentially of preparing the solution of Vitamin D, either as Vitamin D_2 or D_3, in butter oil. When the potency of the D in the oil is proved, the oil is dispersed in milk solids by subjecting it to high-pressure homogenization. The emulsified mixture is subsequently canned and sterilized.

Continuous flow of product is accomplished through installation of Lo-Vats pasteurizers. Vats are stainless-steel-lined and sheathed, equipped with special drives and stainless-steel agitators, and jacketed for both heating and cooling. The can filler used is equipped with sanitary constructed valves in addition to all contact parts of stainless steel.

WATER

For the purpose of this discussion "water" is intended to mean distilled water and natural fresh waters, not sea water, mine waters, etc. They are treated elsewhere.

With respect to water, the rate of attack is accelerated as the dissolved oxygen, carbonic acid, temperature, and acidity are increased and is retarded by the reverse of these conditions. The rate of motion generally accelerates corrosion up to a certain point mainly by bringing more dissolved oxygen to the metal surface. Above a certain velocity, in the case of iron, however, there is a retarding effect due to the more rapid formation of protective layers of corrosion product on the metal. Metal surface films and deposits formed from substances in solution in the water or by corrosion products often determine the rate of underwater corrosion. (Uhlig, H. H., Hot and Cold Water Systems, "Corrosion Handbook," p. 496, John Wiley & Sons, Inc., New York, 1948.)

Iron and Steels.—It is well known that metals differ materially in their resistance to the action of water. In ferrous metals, such as malleable iron castings, wrought iron, soft steel, ingot iron, low-alloy steels, and copper-bearing steels or iron used for water pipes and boiler tubes, no material difference is found in the rate of distribution of corrosion. Higher percentage of alloying elements such as chromium and nickel may increase the resistance to corrosion. Stainless steel such as 18-8 is a notable example. However, this and similar alloys are susceptible to pitting when halogen irons are present in the water. (*Ibid.*)

Aluminum.—Distilled water is not contaminated by contact with most aluminum-base alloys. For this reason, the use of aluminum-alloy storage tanks, piping, valves, and fittings for handling distilled water is fairly extensive and satisfactory.

The action of some tap waters, especially those low in heavy metal salts and chlorides, on aluminum is so nearly negligible that this metal is used successfully for cooling coils, tanks, vats, valves, and piping. The action of those tap waters which are harmful to aluminum can be inhibited readily by the addition of certain chemicals to prevent attack on the metal.

Unpolluted rain waters can be stored and piped in aluminum without fear of attack and contamination. (Aluminum Co. of America, "Aluminum in the Chemical Industry," p. 5, 1944.)

The Alclad products are much more resistant to perforation by pitting than are the other aluminum alloys. Therefore, wherever the characteristics of a specific water are not known in advance, it is safer to employ aluminum alloys such as Alclad 3S. (Uhlig, *op. cit.*, p. 43.)

Aluminum piping up to 6 in. diameter has been used for the distribution of ordinary softened and purified water in rayon plants in order to avoid introduction of any iron rust. This use has been very satisfactory, except where water was inadvertently contaminated by copper dissolved from a heater which had copper pipes in it. The dissolved copper was precipitated on the aluminum pipe and caused local corrosion.

Sometimes in the chemical industry, the chemical to be treated does not corrode aluminum, but the cooling water used in the jacket of the aluminum vessel may do so. In this case, it has been found that the rate of attack can often be greatly reduced by suspending zinc plates in the water adjacent to the aluminum surface and electrically connected thereto. The zinc protects the aluminum and must be replaced from time to time. (Frary, F. C., Aluminum Chemical Equipment, *Trans. A.I.Ch.E.*, Vol. 36, p. 413, 1940.)

Copper.—When heated, certain waters deposit thick mineral scales on the hot metal surfaces. These scales may completely protect the underlying metal. Specimens of copper-base alloys have been examined which were so well protected by carbonate- and silicate-type scales that they have resisted attack for generations.

Copper tubing is now being used extensively for water distribution in chemical plants. Where waters show definite corrosive qualities, red brass is generally used.

Wood.—Both red cypress and redwood are often used for water tanks, since they are remarkable in their resistance to decay. Cypress is the preferred of the two woods.

Saran.—Extensive use has been made of Saran pipe in distilled-water and treated-water systems. It is satisfactory for this purpose except in laboratories, which cannot tolerate even very slight chloride contaminations of the water. It has been found that distilled water on standing in tubing picks up HCl (Saran being a chloride compound). It appears that Saran tubing or pipe can be used in this application, except in the most critical instances, by flushing a line before use if the water has been standing stagnant—and this is no more than good technique no matter what the piping material. (Williams, D. R., Saran Pipes, *Chem. & Met. Eng.*, Vol. 52, No. 9, pp. 112–113, 1945.)

Saran pipe was used for deionized water at the Oak Ridge atomic energy plant. (Schrader, R. J., and A. de Haan, Special Materials Solved Corrosion Problems at Oak Ridge, *Chem. Eng.*, Vol. 53, No. 11, pp. 96–101, 1946.)

Saran pipe carries deionized water at Oak Ridge, Tenn., atomic-energy plant. The method of supporting valves and piping is shown here. It was extensively used for distilled water.

Block-tin pipe has been considered as ideal for transporting distilled water. (Gonser, B. W., Tin, *Food Ind.*, Vol. 7, No. 12, p. 585, 1935.)

Toncan iron resists the corrosive action of boiler-water feed water containing a variety of corrosive substances. Worthite pumps and valves are used with distilled water. Pyroflex linings have been successfully used for water-softener tanks and softened-water storage tanks.

A large New Jersey chemical plant transports soft water to the plant in Transite lines. Duroline is used for feeder lines, and finally copper for the distribution system, while a Baltimore chemical plant uses galvanized pipe throughout. Treated hot-water lines in another plant are steel pipe and valves with a vitrified enamel lining.

Neoprene-impregnated cotton sheeting in large quantity is used to seal the side walls to the floating tops of large tanks handling deaerated water in a plant.

Glass-lined steel is frequently used for the storage of distilled water at room temperature.

Monel possesses excellent resistance to corrosion by waters of all sorts, including distilled water and natural waters, both hard and soft. (Communication from W. Z. Friend.) In distilled and fresh water, rates of corrosion usually are negligible, being less than 0.001-in. penetration and often less than 0.00001-in. penetration per year under the most severe conditions of temperature, flow, and degree of aeration. Monel is the standard material for water-meter parts, feed-water-pump parts, flush-valve parts, well strainers, etc. Considerable quantities are used for hot-water heater tanks.

A spectacular use of Monel, based on its known ability to withstand corrosion and erosion by water, is for the valve seats on the 32-ft.-diameter gate valves which control the flow of water to the turbines at Hoover Dam.

Nickel possesses a very high degree of resistance to corrosion by natural waters and by distilled water. Analysis of distilled water from a nickel storage tank indicated a rate of corrosion of only 0.000001-in. penetration per year. Similarly, tests in natural waters have shown corrosion rates always less than 0.001-in. penetration per year. Nickel is especially resistant to corrosion by waters containing hydrogen sulphide or free carbon dioxide.

Carbonated water is only slightly corrosive toward nickel. Analysis of water from a nickel-lined carbonator operated at a pressure of 200 psi. indicated a rate of corrosion of only 0.0002-in. penetration per year. It has been noted that in the presence of a high concentration of chlorides, as in one case 2,000 ppm., carbonated water may cause pitting of nickel.

Inconel is practically free from corrosion by distilled water and fresh water, including the most corrosive of natural waters which contain free carbon dioxide, iron compounds, chlorides, and dissolved air. It has been chosen for water-handling equipment where the most foolproof material available was desired.

For processing sensitive pharmaceuticals, for preparing photographic materials, and for much analytical work, distilled water is a constant necessity. Fused quartz and platinum are sometimes used for the condenser tubes and receiving vessels when exceedingly pure water is needed. However, for most commercial applications such high purity is generally not required and insignificant amounts of metallic ions can be tolerated. Under these circumstances, pure solid tin or as a lining or coating on a base material has been more commonly employed for distilled-water equipment, including the still, receiver or storage tank, piping, and other accessories. In recent years more attention has been given to other materials of construction, and consequently Monel, nickel, Inconel, and the 18-8 stainless steels are being increasingly applied for various units of distilled-water systems. In addition to the advantage of excellent corrosion resistance, these materials possess strength properties that enhance the convenience and permanence of such installations.

WHISKY

The production of whisky and other distilled liquors varies from one distilling to another, but the differences are not important. All have problems in materials of construction.

Production

Materials of Construction.—A great variety of nonmetallic and metallic materials are in use. Among the more important are stainless steel, copper, Inconel, glass-lined steel, and tinned copper.

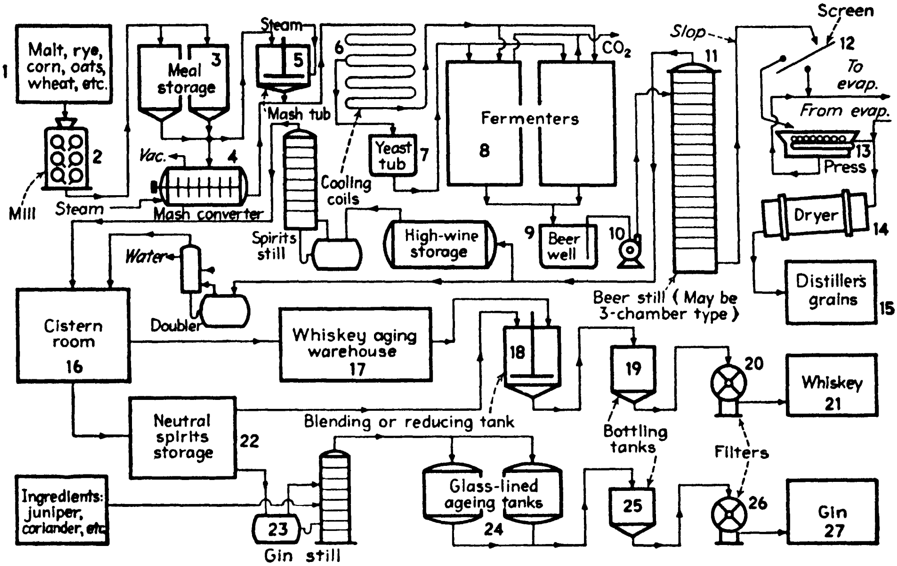
Process.—The truly modern distillery has been designed by distillery engineers. The basic raw materials for distillery operations are corn and rye grains and barley malt. Together with yeast and water, they go to make up the ferment from which the whisky is eventually distilled. The old slow methods of grain unloading have given way to the more efficient, rapid, and sanitary method making use of pneumatic conveyors. Since the grain itself does not pass through the exhausters, they can be constructed of standard materials. The conveyors are generally made of flexible metallic tubing; however, they wear out rapidly owing to the abrasion from the grain. Rubber tubes are somewhat more successful, but under certain conditions, static electricity is developed which is an undesirable condition to foster near combustible dust, although a properly equipped grain-unloading department should have little dust.

Because grain is an expensive material and government regulations require that distillers account for all the grain received, the accurate weighing of grain as it is received is important. There are no unusual problems in this connection except the abrasion from the grain.

Some distilleries are still using wooden bins for grain storage, but these are unsanitary and encourage contamination of the grain, which affects the product. They are being replaced more and more by concrete or welded-steel bins. There is still an opportunity for the development of more satisfactory interior coatings that will prevent the clinging of grain dust to the steel or concrete bins. The latter must necessarily be made watertight in order to prevent sweating and consequent molding of the grain.

Before the grain can be "mashed" for fermentation, it must be ground into a meal. This is usually accomplished by attrition, hammer, or roller mills. These roller mills are generally three-high mills. Uniformity of grinding is one of the most important features of this operation, as it affects the yield. From the mills, the meal is dropped or conveyed into bins. Probably the most modern method of moving the meal from the mills to the bins is the pneumatic system, but screw and redler conveyors are generally used.

The grain meal bins were made of wood in the old distilleries because of the physical limitations of other materials. Then, too, steel causes condensation inside the meal bins with deterioration and molding of grain. However, this objection can be avoided by proper heating and ventilating conditions in the bin room or by suitable insulation. High-grade concrete bins smooth-troweled on the inside, made impervious by waterproofing treatment, and glazed with several



Distilled liquors.

1. Concrete, steel, wood
2. Steel, cast iron
3. Steel, concrete, wood
4. 0.25 per cent copper-bearing steel
5. Copper, 0.25 per cent copper-bearing steel
6. Copper tubes, iron or steel jackets
7. Stainless steel, copper, 0.25 per cent copper-bearing steel
8. 0.25 per cent copper-bearing steel, wood
9. 0.25 per cent copper-bearing steel, concrete
10. Stainless steel, bronze
11. Copper
12. Stainless steel, copper, wood
13. Stainless steel, Ni-Resist, bronze
14. Stainless steel, 3 per cent nickel steel, 0.25 per cent copper-bearing steel, mild steel
15. Steel
16. Inconel, tinned copper, stainless steel
17. Charred oak barrels
18. Inconel, glass-lined steel, tinned copper, stainless steel
19. Inconel, glass-lined steel, tinned copper, stainless steel
20. Inconel, tinned copper, stainless steel, bronze
21. Glass bottles
22. Inconel, tinned copper
23. Inconel, stainless steel, tinned copper
24. Inconel, glass-lined steel, tinned copper
25. Inconel, glass-lined steel, tinned copper
26. Inconel, stainless steel, tinned copper
27. Glass bottles

coats of Bakelite varnish on the inside provide the ideal type of bin where bin weight is not a problem.

The grain meal is moved by a combination of screw conveyors and gravity to either mash tubs or pressure cookers, where the starch is put into solution by cooking with water. The open-type mash tub is rapidly being superseded by the pressure cooker. This is because the latter, a closed vessel, can be easily sterilized. These cookers operate by the introduction of steam directly into the mash through the bottom of the mass of grain meal and water. Continuous mashing and converting apparatus is being used by several distilleries at this time.

The distiller may hold the mash in the mash tub until the conversion process is complete or may transfer it to another holding vessel, called a "drop tub" or "converter," which holds the mash until the conversion is complete. When the pressure cooker is used, the malted grain is generally added to the mash after it has been thoroughly pastified and cooled to the proper malting temperature.

The malt is thoroughly mixed into the mash by the cooker's agitator, and then the entire mash is transferred to a drop tub or converter to be held until conversion takes place. The drop tubs are subjected to a pH of 4.0 to 5.5, and the percentage of acid as lactic ranges from 0.23 to 0.53 per cent, with a temperature range of 125 to 145°F. While the acid concentration is not high, these converting vessels should be made of low (approximately 0.25 per cent) copper-bearing steel for long life. These converters are, of course, equipped with mechanical agitators to accomplish thorough mixing.

In either the mash-tub or pressure-cooker method, the converter or drop tub may or may not be equipped with cooling coils. If it has cooling coils, the mash can be cooled in the converters to the proper temperature for filling the fermenters. If the converters are without cooling coils, the mash is pumped through mash-cooling devices, generally double-pipe coolers of the counterflow type, and thence into the fermenters. A recent development is the continuous vacuum mash cooler.

Mash coolers are probably the most inefficient equipment around a distillery. Since an acid corrosive condition exists in the mash and because of sanitary requirements, the inner tube of the double-pipe mash coolers is generally made of hard-drawn copper while the outer pipe is of iron or steel tubing for sake of economy. This tends to set up an electrochemical action between the copper and the steel.

The pumps used for forcing the mash through the coolers and into the fermenters are of various types, the constant-displacement type being most common. In the duplex steam pump as well as the motor-driven duplex pump with variable-speed drive, the variable range of speed and therefore variable rate of feed are sometimes desirable. Such pumps, like the rest of the equipment, must be easily sterilized. All parts of mash pumps coming in contact with the mash should be made of bronze, copper, or stainless steel.

The mash is pumped from the coolers into fermenters. Years ago, wooden fermenters were found to be far from ideal, but because of low cost and other reasons, practically all distilleries used this type. Most distilleries are replacing wood with metal fermenters. The acidity present in fermenters causes more or less corrosion. Lactic acid concentrations up to 1.8 per cent, carbon dioxide, and sometimes high temperatures are involved. Iron or steel fermenters seldom last more than 10 years. The more modern installations are made from copper-bearing steel (approximately 0.2 to 0.25 per cent copper), with welded butt joints ground smooth. Copper or stainless-clad steel would be satisfactory, but the cost is too great.

Since truly modern fermenters have attemperating coils, generally made of copper, hung on steel or brass rods, there is the possibility of electrochemical action. With ordinary plate fermenters this can be quite serious. When copper-bearing steel is used, the copper tends to hold the oxidized iron on the surface of the steel, thereby tending to produce a film which greatly retards the corrosion rate. Experiments have been made to spray tin on steel fermenters, but the cost is excessive for the large surfaces to be covered. Another important point in the construction of metal fermenters is the provision for good drainage so that no material can remain to decompose. Such material courts destruction.

The modern distillery is equipped with closed-top fermenters to permit pressure sterilization with steam and to permit the recovery of the carbon dioxide gas. The gas is passed through scrubbers in order to remove any entrained alcohol. These scrubbers will last only a few years. In one case, a steel shell scrubber with cast-iron plates lasted only 39 months.

Machines for developing pure culture yeast should be made of stainless steel, copper, or copper-bearing steel. The yeast-growing vessels equipped with agitators and cooling coils and the conditions to be encountered are quite similar to the problems to which the fermenters are subjected. This is likewise true of the large vessels, which are sometimes called "beer wells," into which the completely fermented mash is conveyed and from which it is later fed to the stills by centrifugal or piston pumps. All such vessels should be made of copper-bearing steel (with a minimum of 0.20 per cent copper, 0.5 per cent is very desirable) or concrete.

Various types of stills are used for the production of different whiskies, but practically every one is made of copper. This metal seems to satisfy the demands for resistance to corrosion, ease of fabrication, and good heat transfer. Some engineers contend that copper acts as a catalyst in the distilling process and that other metals might contaminate the whisky. Whether these contentions are correct or not, no one has constructed a whisky still from stainless steel, aluminum, etc. The use of these materials should offer some interesting possibilities.

It is necessary to avoid contamination of the whisky with copper, iron, or other metals, because these metals will form precipitates after the whisky is aged and bottled. Inconel, tin, glass, and some stainless steels are good construction materials. Special rubber hose can be used for pipe lines. This problem of metal contamination must be avoided in the still receiver tanks and in the bottling plant because 1 ppm. of iron will darken whisky and cause a precipitate. Other metals have the same effect at high concentrations.

After the distillation process has been completed, the residue, or spent mash, is pumped to the dryer plant for the recovery of the grain solids, which are sold as stock feed. The spent mash contains about 5 per cent solids. It is at a temperature of 220°F. A typical analysis includes lactic acid, 0.25, and ash, 0.135 per cent.

The recovery process generally starts with a screening of the spent mash to recover as much of the solids as possible. Perforated copper sheets or woven-wire screens are satisfactory if they are structurally strong enough. Stainless steel is satisfactory for this purpose; in fact, it is the most valuable material in connection with this step in the operations. The screen frames may be made of wood, but even cypress or cedar soon falls apart under the conditions encountered.

After the spent mash has been screened, the recovered solids are conveyed to a dewatering press for further removal of moisture and then sent to a drying system. Water from the screens goes to evaporators, where it is reduced to a sirup of 25 to 45 per cent solids for combination later in drying machines, with the solids originally removed by the screens, or for drying on drums or in spray dryers for a special product. In one installation, the effluent from the screens is centrifuged to remove a large portion of the suspended solids and thus lessen the evaporator load to one of dissolved solids only.

Since both the screened material and the effluent are at a temperature of about 200°F. and contain 0.25 per cent acid as lactic, the corrosion problem of all equipment involved is serious. The machines generally used for drying the grain solids and combining the sirup from the screen effluent to make the feed are the rotary steam tube type operating with forced draft and sometimes both forced and induced draft. In the induced-draft fan system, a severe condition of corrosion at relatively high temperatures is set up, plus a plentiful supply of oxygen, which follows with the high velocity of the air used to create the draft. Since the feed at some steps in the process is in solid form, it is generally moved by screw conveyors, hoppers, chutes, etc., upon which are imposed severe corrosion conditions.

Dewatering presses not only have to handle the screened material at 200°F., but are generally surrounded by vapors saturated with the acid from the material. All parts of these presses should be made of stainless steel and bronze, with castings of austenitic cast iron such as Ni-Resist. Dewatering presses made of ordinary cast iron and steel will generally not last more than 2 years under a 24-hr.-day operation. Where stainless steel is not economical, air duct and stacks made of Transite or similar cement and asbestos combinations seem to be about the best solution at the present time. Since fans are not obtainable in Transite, the most satisfactory material available to date seems to be 18-8 stainless steel.

Although 5 per cent nickel will not stand the vapor handling, it is, curiously enough, satisfactory for the shells of the rotary drum dryers, possibly because the surface of the interior of the shell becomes coated with a protective film of dried feed and bits of sirup. However, in the dryers the moisture content of the feed is low and the moisture in the air is generally considerably below the saturation point. Possibly for the same reason, the steam tubes of these dryers can be of ordinary mild carbon steel with a life expectancy of 8 to 10 years.

Centrifuges, when used, should have stainless-steel-clad shell and stainless-steel or bronze baskets, the former being the more desirable.

The evaporators handle the thin effluent from the spent mash after it has passed through the steps of screening and/or centrifuging, concentrating this liquor to about 25 to 50 per cent solids. A typical analysis at this stage includes slightly over 8 per cent lactic acid and 3.65 per cent ash.

Cast-iron evaporator bodies are used because of the high cost of other materials. An extra-heavy cast-iron shell can be secured at a much lower first cost than any other material. Copper steam chests, however, are a good investment. Silicon copper or stainless steel would be better construction materials for evaporators, particularly for high-velocity evaporators. Anyone who has tried to use ordinary steel or iron piping for evaporator service on the material discussed here has learned that all such piping must be replaced with brass, copper, or other noncorrosive material after 12 to 18 months of service.

The dried feed is generally stored awaiting shipment in bins and can be as warm as 120°F. but preferably below 100°F. Ordinary galvanized sheet-metal bins are "money thrown away"; in fact, galvanized iron or sheet metal should not be used at any place in a plant of this type. Good black-iron sheets of commercial purity are thoroughly satisfactory for grain storage bins, although it is doubtful if they will last more than 5 to 7 years under 24-hr. per day operation when warm feed is stored in them. Some distilleries avoid storing dried feed in bins by cooling the material from the dryers and bagging it immediately.

Mixing and other conveyors handling the feed in various conditions of moisture content should be made of muntz metal. (Weiner, L. P., *Chem. & Met. Eng.*, Vol. 44, No. 12, p. 710, 1937; and Vol. 45, No. 1, p. 32, 1938.)

In preparing grain mashes in pressure cookers, heat is available for conservation at the time the pressure is relieved. In order to save the heat, a blowdown heat exchanger was installed to heat water for process purposes. It is a bent-tube type. Arsenical copper tubes to date have given no trouble.

Last but not least in the scale of corrosion problems about a distillery is that of return pipe carrying condensate. The problem in general is no different from that encountered in any large central heating plant wherein all steam used for heating purposes is condensed. Naturally the composition of the steam greatly affects the life of such piping systems. Deaeration should be used wherever possible to reduce the free oxygen in all the water entering the system to at least a maximum of 1 cc. per l. After heating the water for any supply purposes, the balance of the free oxygen should be removed if possible by further deaeration. It must be remembered a small amount of carbon dioxide may do considerable damage, as it may be driven off as a gas with the steam and redissolve in the condensate, forming carbonic acid water which attacks iron. When the condensate is conserved, returned, and reheated, this cycle can be carried on indefinitely with a small amount of carbon dioxide doing a considerable amount of damage to all metals coming in contact with the condensate.

Inconel and Inconel-clad steel are now considerably used for whisky blending and bottling tanks and bottling lines where bonded whiskies are blended with neutral spirits or handled as straight bonded whiskies. The principal consideration is prevention of any effect on whisky color during fairly long contact periods.

WINES

Use of metals in the production and distribution of wine faces two problems, namely, corrosion and the effects of metals on flavor, physiological action, keeping qualities, and other properties of wine. The principal effects of the metals on wines concern color and sparkle. The influence of flavor and bouquet is much smaller for a given concentration of dissolved metal. The highest permissible concentrations of various metals in wine (causing no particular change) are as follows, in milligrams per liter: iron, 1; tin, 1; chromium, 15; copper, 60; aluminum, 100; zinc, 200; nickel, 200. (Muller, R. W., Metals in Wineries, *Korrosion u. Metallschutz,* Vol. 14, p. 385, 1938.)

Production

Materials of Construction.—Very few metals are resistant to corrosion under all conditions existing in a winery. In choosing a metal, therefore, the only safe criterion for selection is a test conducted in the winery at the place where the metal is to be used. Although the safest procedure is to use the most resistant metal indicated by such tests, it is not always the most feasible method. In many instances it is possible to use the less resistant metals in the winery provided they are used where they come in contact with the juices and wines during the early stages of manufacture. This is possible because much of the iron content of musts is lost during fermentation and storage. (Mrak, E. M., D. C. Caudron, and L. Cash, Effects of Certain Metals and Alloys on Claret and Sauterne Type Wines from Vinifera Grapes, *Food Processing,* Vol. 2, pp. 539–547, 1937.)

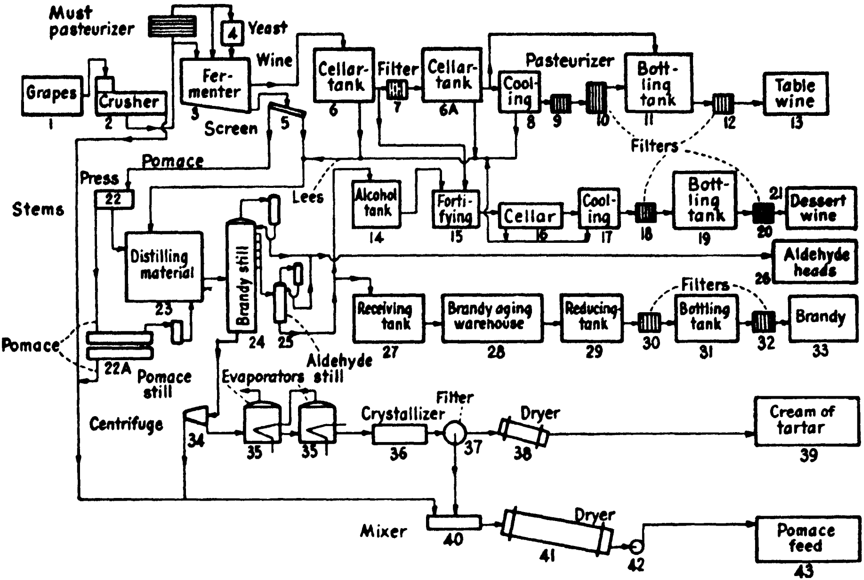
Reasonably resistant metals are safe to use during crushing and fermentation, but only the most resistant metals should be used in contact with stored and finished wines.

Corrosion is greatest at the crushers owing to greater aeration, rigidity of flow, and freshness of fruit. Metals having greatest resistance here are stainless steels, cupronickel, and Inconel. Those having least resistance are cast iron, steel, tin, Ni-Resist, and nickel. At the filter charger, corrosion is also considerable owing to agitation, erosion, and aeration. Again the stainless steel and Inconel are most resistant.

These results are confirmed by another worker in the field. Comparative tests were made with aluminum, tin, copper, nickel, Monel, Inconel, and 18-8 stainless steel. (Muller, *loc cit.*)

There was no measurable corrosion of Inconel or stainless steel. Tin was corroded rather severely, especially by red wines when aeration was poor, and was least suitable of all the tested metals for any equipment where contact was prolonged as in storage. Nickel served well for pipes, juice containers, mixing vats, open fermenters, and the reservoirs of bottle-filling machines.

Stainless steel is excellent for nearly all equipment but less satisfactory for closed fermenters and for juice containers and other equipment not exposed to prolonged contact.



Wine and brandy.

1. Stainless steel and bronze, wood and concrete troughs
2. Stainless steel, bronze
3. Wood, concrete
4. Stainless steel
5. Stainless steel, bronze, copper
6. Wood, concrete, glass-lined steel
7. Type 316 stainless steel
8. Wood, Type 316 stainless steel, glass-lined steel
9. Type 316 stainless steel
10. Wood, Type 316 stainless steel, glass-lined steel
11. Glass, Type 316 stainless steel
12. Type 316 stainless steel
13. Glass, Type 316 stainless steel
14. Tinned copper, Inconel, stainless steel
15. Wood, Type 316 stainless steel, glass-lined steel
16. Wood, concrete
17. Wood, Type 316 stainless steel, glass-lined steel
18. Type 316 stainless steel
19. Wood, Type 316 stainless steel, glass-lined steel
20. Type 316 stainless steel
21. Glass, Type 316 stainless steel
22. Stainless steel, bronze

22*a*. Stainless steel, bronze

23. Wood, concrete
24. Copper, Type 316 stainless steel, tinned copper
25. Copper, Type 316 stainless steel, tinned copper
26. Copper
27. Tinned copper, Inconel, stainless steel
28. Oak barrels
29. Inconel, tinned copper, stainless steel
30. Inconel, stainless steel
31. Inconel, tinned copper, stainless steel, glass-lined steel
32. Inconel, stainless steel
33. Glass, Inconel, stainless steel
34. Stainless steel, bronze
35. Copper, stainless steel
36. Copper, stainless steel
37. Bronze, stainless steel
38. Steel, bronze, stainless steel, Monel
39. Steel, wood, bags
40. Stainless steel, bronze
41. Steel
42. Steel
43. Steel, wood, bags

The facility with which pumps, bottling machinery, cooling coils, and vats made of stainless steel can be switched from one kind of wine to another is a decided convenience, particularly when changing from red to white wines. All color of wine can be quickly washed from the surface of stainless steel. (Mitchell, W. M., Steel Alloys, *Food Ind.*, Vol. 7, No. 12, pp. 577–579, 1935.)

But a word of caution is advisable. In wines or spirits containing a very high content of tannic acid or tannin compounds, the use of 18-8 for long periods of storage may be inadvisable because of the reaction with the iron, which may induce discoloration and turbidity. The use of a stabilized 18-8 is advisable for all welded equipment. (*Ibid.*)

Redwood has been in use for many years for wine storage tanks. Its lack of characteristic taste or odor makes it especially suitable for tanks and vats. It is good for either red or white wines. (California Redwood Association, *Tech. Bull.* T 16–11.)

Wines have no effect on concrete, but their tastes may be affected by it. To overcome this the concrete can be treated with several applications of tartaric acid solution or sodium silicate. Some wineries, producing fine wines, line concrete tanks with glass tile. (Boase, A. J., Concrete for Structures and Equipment, *Food Ind.*, Vol. 7, No. 12, p. 589, 1935.)

Concrete has become prominent in large California wineries for fermenter, cellar, and cooling tanks. These have given fair service when a coating of calcium tartrate has protected the surface. Calcium in wine will often form a precipitate in the bottled wine, similar to the action of iron, copper, and aluminum. Of a number of coating materials that have been used for protecting concrete tanks from the action of wine, microcrystalline wax, applied hot, appears to be one of the best. (Communication from E. C. Pattee.)

Rubber wine hose is used for handling wine in various stages of manufacture and for filling barrels with wine.

Wine is often pumped with all-bronze or 18-8 Cb stainless-steel pumps. Pipe lines made of cellulose acetate butyrate plastic have been used for several years for carrying wine in one plant. Large volumes of wine have been pumped through the lines—dry wines, sweet wines, wines with low alcoholic content, wines with 20 to 24 per cent alcohol, wine heated at 112°F., and wine cooled down to 18°F.

The plastic lines have withstood the broiling suns of summer and the chilling cold of winter within a temperature range extending from below zero to possibly as high as 110°F. With the exception of temporary slight distortions due to contraction and expansion, the lines have behaved quite satisfactorily without sustaining permanent deformities.

A number of wineries have large installations of glass-lined steel storage tanks, with no corrosive effect occurring.

Inconel and Inconel-clad steel can be used in wine-making processes. They are satisfactory for those locations where wines or grape juices must be stored over long periods of time. Champagne mixing tanks, wine processing tanks, and wine storage tanks are fabricated regularly from Inconel and Inconel-clad steel.

Inconel tubing is used in wine heaters and pasteurizers, for cooling coils circulating refrigerants in the cooling of champagne during processing, and in wine siphons. Special valve seats fabricated from Inconel rod have been used in valves handling grape wine in process.

Pure nickel is used in wine bottling tanks, in continuous wine coolers, and in batch pasteurizers. Tubing of nickel is used in wine coolers, in champagne mixing tanks, and in wine siphons.

Among the established applications for Monel in the winery are filter cloth and other parts of wine filters, linings for wine-blending tanks, and tubing of cooling coils in wine process tanks. Monel funnels, set below the grape crushers, are used to collect grape juice, which is conveyed through Monel tubing to the fermenters. (International Nickel Co., Metals and Wines, Distilled Liquors and Beers, *Bull.* TS-6, 1939.)

Process.—Production, in general, has been considerably improved by modern equipment and some new techniques. (Cruess, W. V., and C. R. Havighorst, How California Wines Are Made, *Food Ind.*, Vol. 20, No. 4, pp. 522–530, 1948.) The grapes are crushed in an Italian-type crusher-stemmer. They drop through holes in the cylinder into the sump, and the stems are kicked out of the open end of the machine.

Crushed grapes are pumped from the sump through a pipe to the vat. This pipe should be of stainless steel, but it is more often of plain steel or copper. While some metal is picked up by the must, it is believed that most of it is precipitated during fermentation with the yeast.

Sulphur dioxide is added in the crushing vat as a solution of SO_2, as a gas, or as a bisulphite. All these forms are satisfactory.

In the making of white table wines and Angelica, also Muscatel in some plants, the freshly crushed grapes are allowed to drain into a concrete sump and the resulting juice is pumped to a fermentation vat, oval, or tank. Fermentation vats are open, circular redwood tanks of rather shallow depth or are rectangular open concrete tanks.

Tanks are either of redwood or of concrete. They differ from the usual fermenter in being covered and are usually deeper and larger.

Ovals are usually of oak. They are used for fermentation and aging of white table wine.

Pumps should be made of corrosion-resistant bronze or of stainless steel, since traces of iron and copper cause haziness in white wines.

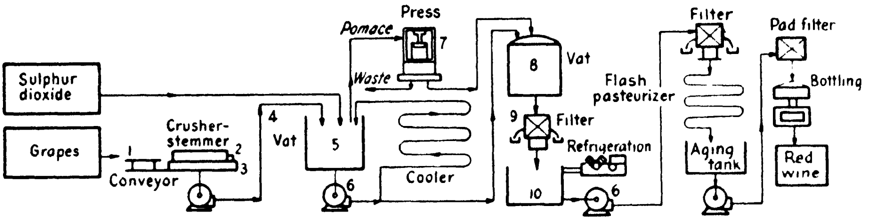
Wine filters are of several types; the two most common are plate-and-frame filter presses of customary design and the screen plus infusorial earth filters, in which a layer of filter aid is built up on hollow leaves made up of very fine screens of stainless steel or other corrosion-resistant alloy. Plate-and-frame filters are made of aluminum or aluminum bronze, stainless steel, or other corrosion-resistant material.

For finishing or "polishing," a plate-and-frame pad filter in which asbestos pads are held between metal frames is generally used. Unglazed porcelain candle filters and also wood-pulp filters have been used but have been largely replaced by plate-and-frame or screen filters.

At present stainless steel, aluminum, or aluminum alloy is used in pasteurizers. And instead of the old tubular heaters and interchangers, hollow plate pasteurizers have been installed to replace the old copper outfits. Also, beyond the pasteurizer is usually a stainless-steel holding chamber to increase the plate pasteurizer's capacity and to ensure thorough pasteurizing.

The new wines are chilled by passage through the tubes of a direct freon- or ammonia-cooled refrigeration machine. Wines are then bottled by means of stainless-steel fillers.

Red Table Wine.—In making red table wine the flow sheet is about as follows: The grapes are crushed, stemmed, and pumped to fermentation vats; given about 100 to 150 ppm. of SO_2, a 2 to 3 per cent starter of must fermenting with pure yeast, and the vat is pumped over or punched two or three times daily to help extract the color of skins and to prevent acetification in the "cap" (top layer of skins). It is tested three times daily for Balling degree, and the temperature maintained below 85°F. by occasional countercurrent cooling. The free run juice is drawn off at about 0 to 2° Balling (when color extraction is sufficient), the pomace is pressed, and the press wine is added to a vat of freshly crushed grapes. The free-run wine is fermented out bone dry in a covered storage tank which is entirely filled and closed after fermentation is complete. The wine is racked when well settled (November and December) into another tank or into oak barrels or puncheons for aging for 2 to 4 years. It is racked in each fall or winter and spring, filtered or fined, refrigerated, aged, flash pasteurized, filtered or fined, and bottled or barreled. If bottled, the wine is stored in bins 6 months or longer to "mellow up" and so that the vintner can determine if it will "hold up" in the bottle.



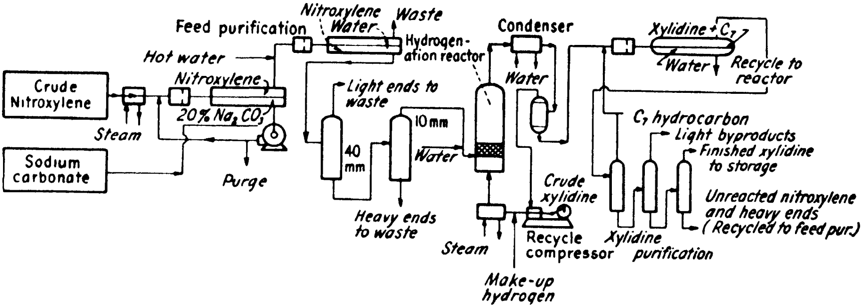
Red wine.

1. Concrete and wood trough, bronze and iron chains
2. Stainless steel, copper, bronze
3. Concrete
4. Stainless steel, copper, carbon steel
5. Redwood, concrete
6. Stainless steel, bronze
7. Stainless steel, bronze
8. Wood, concrete
9. Aluminum, stainless, bronze
10. Wood, concrete
11. Aluminum, stainless, bronze
12. Stainless steel, bronze
13. Aluminum, stainless steel, glass
14. Stainless steel, wood
15. Asbestos pad

White Table Wines.—Procedures vary somewhat; the following is a composite flow sheet for white wines of ordinary quality. Crush and stem, pump to vat, add SO_2, drain off free run, press the pomace and keep press juice separate, ferment both with pure yeast in ovals or covered tanks, cool as necessary to keep temperature below 70°F. From this point handle as outlined for red table wine.

XYLIDENE

Materials of Construction.—Selection of materials of construction is exceptionally simple, as there are no problems involved. Ordinary carbon steel can be used throughout in processing equipment. In the reactor circulating system, copper-containing alloys must be avoided because of ammonia formed as a reaction side product. Here again, ordinary carbon steel is satisfactory.



Xylidine. Ordinary carbon steel can be used throughout. In the reactor circulating system, copper-bearing alloys must be avoided because of ammonia formed as a reaction side product.

Process.—Xylidines have been made by batch processes for years. Recently a continuous catalytic hydrogenation method was developed by the Shell Development Co. (De Largey, R. J., J. P. Okie, and L. M. Roberts, New Xylidene Process Revealed, *Chem. Eng.*, Vol. 55, No. 10, pp. 124–126, 1948.)

Xylene was nitrated to nitroxylene. The nitrophenolic by-products in the crude nitroxylene were removed by treating with hot soda ash solution in a steel mixer-settler system. Light hydrocarbons and dinitroxylenes were next removed by fractionation.

The purified nitroxylene was hydrogenated in catalytic reactors using nickel on an inert carrier. The exit stream, rich in crude xylidene, was condensed in ordinary water-cooled exchangers and stored for purification by distillation.

The crude product was refined in a series of three distilling columns. The first column removed the C_7 hydrocarbon, previously introduced for phase separation, as a top cut. The second column removed the light by-products. Finished product was taken off the top of the third column. It was inhibited with 0.01 per cent of an alkylated phenol to prevent discoloration or gum formation; it was stored under a nitrogen atmosphere.

ZINC CHLORIDE

The production and handling of zinc chloride are both sources of corrosion troubles if the proper materials of construction are not used.

Production

Materials of Construction.—Brick-lined or glass-lined steel can be used for the dissolving tank. Rubber-covered equipment is being used for some applications. The saturated zinc chloride solution is stored prior to shipping in rubber-lined or lead-lined tanks.

Fumes given off from the dissolving tanks were formerly carried outside in a wooden flue, which usually fell apart in less than 4 months. The wooden flues have been replaced with Transite Type S, and the condition of these still appears good after 1.5 years at one plant.

The corrosion engineer in a plant making zinc chloride has found a rubber-covered agitator used in a dissolving tank very satisfactory. The agitator had been a perpetual source of trouble. Formerly the agitator had been made of wood and usually lasted no more than a few months. Thought had been given to the use of a steel assembly coated with hard rubber, but the heat of reaction kept the temperature close to 100°C. No rubber manufacturer would guarantee such an installation because of the high temperature, although rubber is well known for its resistance to hydrochloric acid at low temperatures. Several rubber samples were investigated. The trial agitator, constructed of steel coated with hard rubber, has been in service for 1.5 years and shows no signs of deterioration. The rubber used is one of the Flexlastic synthetic rubber compounds.

Process.—This plant is making zinc chloride from a zinc sludge (metallic zinc and zinc oxide) by dissolving the sludge with concentrated hydrochloric acid, filtering, and evaporating the resulting filtrate to the desired concentration of zinc chloride. The dissolving tank is brick-lined steel and is equipped with a rubber-covered steel agitator. The saturated solution is stored in lead or rubber-lined tanks depending upon the customer's lead or iron tolerances.

Handling

Copper tubes have found preference in evaporators handling zinc chloride. (Wright, A. G., *Chem. Age*, p. 438, June 10, 1939.)

This chemical can be pumped by stabilized 18-8 Mo or higher chrome-nickel stainless steels or by high-silicon iron. The last has been used in zinc chloride solutions from 15 to 73°Bé. at temperatures up to 140°C. Durimet 20 is resistant to the chloride at all temperatures and concentrations. Both hard and soft rubber are used.

Worthite equipment is in plant service. Lead has been used. Karbate can handle a solution of any concentration up to the boiling point. Illium in zinc chloride at 70°F. shows not more than 0.004-in. penetration per year.

Monel tubes have overcome troublesome corrosion in an evaporator in a fiber mill which treats certain of their papers with zinc chloride. This chemical is recovered by evaporation from the wash waters of the treating process. A plant which concentrates zinc chloride wash liquors of 10 to 30°Bé. strength to 70° in a double-effect vacuum evaporator found the corrosion rate of Monel to be only 0.0045-in. penetration per year. Monel-covered dryer rolls are used in contact with zinc chloride-treated fiber. (International Nickel Co., *Bull.* C-3, p. 31, 1938.)

At the Wheatland Tube Co.'s plant at Wheatland, Pa., there is a plant converting pickle liquor into ferric hydrate, zinc sulphate, and zinc chloride. (Kraiker, H., Jr., Dispose of Pickle Liquor at a Profit, *Chem. Eng.,* Vol. 56, No. 3, pp. 112–115, 1949.) The keynote of the process is resistance to chemical corrosion. All the process piping is Monel; all the equipment is either glass-lined or Monel. The pipe lines and equipment associated with the chlorination reactor presented a special problem. Hastelloy C is used where glass or glass-lined steel could not be used. All the jackets and most of the packings are Teflon.

Packaging

Zinc chloride is shipped in lead or rubber-lined containers.

ZINC SULPHATE

Aqueous solutions of most of the inorganic acid sulphates hydrolyze to a certain extent to form dilute sulphuric acid, particularly at temperatures associated with their evaporation. (Friend, W. Z., Corrosion by Sulphates, *Chem. Eng.,* Vol. 55, No. 11, pp. 145–147, 1948.) Some of them contain free acid in the crystalline salt. When the solution is acid, a metal resistant to dilute sulphuric acid can be used such as lead, copper, bronze, or Monel. A neutral solution can be handled by ordinary materials such as cast iron and steel.

Among the other materials useful with zinc sulphate are stainless steels, Hastelloys, nickel, Inconel, Durimet, Worthite, hard and soft rubber, and Karbate. Monel has useful resistance to solutions of most of the nonoxidizing acid sulphates and has numerous applications in the evaporation and handling of such solutions. (*Ibid.*) Nickel and Inconel usually are somewhat less resistant than Monel in the hot solution though having a number of applications where special conditions, such as necessity for freedom from copper pickup by the solution, dictate their use. The Ni-Resist alloy can be used with some of the more dilute acid solutions and usually are considerably more resistant than cast iron. Examples include the use of Monel evaporators or evaporator or heater coils and tubes for zinc sulphate. Monel-lined rotary dryers are used for drying zinc sulphate.

DIRECTORY OF MATERIALS

This directory provides a quick means of identifying materials available for the construction of chemical-plant equipment. Materials are arranged alphabetically within each of six classes of materials. (From November, 1948, issue of *Chemical Engineering* and copyrighted by McGraw-Hill Publishing Company, Inc.)

Materials	Manufacturer	Description
	Metals and alloys	
Acipco Stainless	Amer. Cast Iron Pipe Co., Birmingham, Ala.	Various standard stainless steels
Admiralty	Generally available *	70 Cu; 1 Sn; 29 Zn
Admiralty, Antimonial	Chase Brass & Copper Co., Waterbury, Conn.	71 Cu; 27.95 Zn; 1 Sn; 0.05 Sb
Admiralty, Arsenical	Generally available *	71 Cu; 28 Zn; 1 Sn; 0.04 As, Sb or P
Admiralty, Phosphorized	Scovill Mfg. Co., Waterbury, Conn.	71 Cu; 28 Zn; 1 Sn; 0.03 P
Advance	Driver Harris Co., Harrison, N.J.	55 Cu; 45 Ni
Alchrome 3	Wilbur B. Driver Co., Newark, N.J.	Fe; 20 Cr; 3 Al
Alchrome 6	Wilbur B. Driver Co., Newark, N.J.	Fe; 20 Cr; 6 Al
Alcoa 99.6 Al	Aluminum Co. of Amer., Pittsburgh, Pa.	99.6 Al
Alcoa 2S	Aluminum Co. of Amer., Pittsburgh, Pa.	99.2 Al min.
Alcoa 3S	Aluminum Co. of Amer., Pittsburgh, Pa.	Al; 1.2 Mn
Alcoa 4S	Aluminum Co. of Amer., Pittsburgh, Pa.	Al; 1.2 Mn; 1 Mg
Alcoa 52S	Aluminum Co. of Amer., Pittsburgh, Pa.	Al; 2.5 Mg; 0.25 Cr
Alcoa 61S	Aluminum Co. of Amer., Pittsburgh, Pa.	Al; 0.25 Cu; 0.6 Si; 1 Mg; 0.25 Cr
Alcoa 63S	Aluminum Co. of Amer., Pittsburgh, Pa.	Al; 0.4 Si; 0.7 Mg
Alcoa Alclad 3S	Aluminum Co. of Amer., Pittsburgh, Pa.	3S clad with 72S (Al; 1 Zn)
Alcoa Alclad 4S	Aluminum Co. of Amer., Pittsburgh, Pa.	4S clad with 72S (Al; 1 Zn)

NOTE: Many of the names listed here in the "Materials" column are trademarks and are not to be understood by presentation here to denote generic or descriptive names for general use.

* "Generally available" copper alloys may be obtained from such companies as the following: American Brass Co., Waterbury, Conn.; American Metal Co., New York, N.Y.; Ampco Metal Inc., Milwaukee, Wis.; Bridgeport Brass Co., Bridgeport, Conn.; Bristol Brass Co., Bristol, Conn.; Chase Brass & Copper Co., Waterbury, Conn.; Mueller Brass Co., Port Huron, Mich.; New England Brass Co., Taunton, Mass.; Phelps Dodge Copper Products Corp., New York, N.Y.; Revere Copper & Brass, Inc., New York, N.Y.; Riverside Metal Co., Riverside, N.J.; Scovill Mfg. Co., Waterbury, Conn.; Seymour Mfg. Co., Seymour, Conn.; Wolverine Tube Co., Detroit, Mich.

Materials	Manufacturer	Description
Alcoa Alclad 53S	Aluminum Co. of Amer., Pittsburgh, Pa.	53S (Al; 0.7 Si; 1.3 Mg; 0.25 Cr); clad with high purity Al
Alcoa 43	Aluminum Co. of Amer., Pittsburgh, Pa.	Al; 5Si
Alcoa 214	Aluminum Co. of Amer., Pittsburgh, Pa.	Al; 3.8 Mg
Alcoa B214	Aluminum Co. of Amer., Pittsburgh, Pa.	Al; 3.8 Mg; 1.8 Si
Alcoa 356	Aluminum Co. of Amer., Pittsburgh, Pa.	Al; 7 Si; 0.3 Mg
Allegheny Metal	Allegheny Ludlum Steel Corp., Brackenridge, Pa.	Various standard stainless steels
Aloyco-20	Alloy Steel Products Co., Linden, N.J.	Fe; 19–21 Cr; 28–30 Ni; 4.0–4.5 Cu; 2.5–3.0 Mo; 1.5 max. Si; 0.65–0.85 Mn; 0.07 max. C
Alumel	Hoskins Mfg. Co., Detroit, Mich.	94 Ni; 4 Al; 1 Si; 1 Mn
Ambraloy 901	Amer. Brass Co., Waterbury, Conn.	95 Cu; 9 Al
Ambraloy 917	Amer. Brass Co., Waterbury, Conn.	82 Cu; 9.5 Al; 5 Ni; 2.5 Fe; 1 Mn
Ambraloy 927	Amer. Brass Co., Waterbury, Conn.	
American stainless	Amer. Steel Foundries, Newark, N.J.	Various standard stainless steels
A Metal	Midvale Co., Philadelphia, Pa.	Fe; 19 Cr; 35 Ni; 0.35 C; 1 Si; 0.5 Mn
AMF	Midvale Co., Philadelphia, Pa.	Fe; 46 50 Ni; 0.1–0.2 C; 1–2 Mn
Ampco 8	Ampco Metal, Inc., Milwaukee, Wis.	Cu; 7.5 Al; 2–2.5 Fe
Ampco 12	Ampco Metal, Inc., Milwaukee, Wis.	Cu; 8.5–9.3 Al; 2.5–3.25 Fe
Ampco 15	Ampco Metal, Inc., Milwaukee, Wis.	Cu; 9–10 Al; 2.75–3.75 Fe
Ampco 16	Ampco Metal, Inc., Milwaukee, Wis.	Cu; 9.6–10.3 Al; 3–4 Fe
Ampco 18	Ampco Metal, Inc., Milwaukee, Wis.	Cu; 10.3–11 Al; 3.0–4.25 Fe
Ampcoloy 40	Ampco Metal, Inc., Milwaukee, Wis.	Cu; 9.5–10.5 Al; 0.20 max. Fe
Ampcoloy 45	Ampco Metal, Inc., Milwaukee, Wis.	Cu; 9.7–10.9 Al; 2.0–3.5 Fe; 4.5–5.5 Ni; 1.5 max. Mn
Ampcoloy 49	Ampco Metal, Inc., Milwaukee, Wis.	Cu; 6.5–9 Al; 4 max. Fe; 2 max. Mn
Ampcoloy 62	Ampco Metal, Inc., Milwaukee, Wis.	55–60 Cu; 0.5–1.5 Al; 0.4–2.0 Fe; 1.5 max. Mn; 1.0 max. Sn; 0.4 max. Pb; 0.5 max. Ni; bal. Zn
Ampcoloy 66	Ampco Metal, Inc., Milwaukee, Wis.	60–68 Cu; 3–7 Al; 2–4 Fe; 2.5–5 Mn; 0.5 max. Sn; 0.2 max. Pb; 0.5 max. Ni; bal. Zn
Ampcoloy A3	Ampco Metal, Inc., Milwaukee, Wis.	Cu; 9–10 Al; 1.25 max. Fe
Ampcoloy E123	Ampco Metal, Inc., Milwaukee, Wis.	Cu; 9.5–11 Al; 1.5 max. Fe
Antaciron	Worthington Pump & Machinery Corp., Harrison, N.J.	Fe; 14.5 Si
Armco	Amer. Rolling Mill Co., Middletown, Ohio	Various standard stainless steels
Asarco Acid lead	Amer. Smelting & Ref. Co., New York, N.Y.	Pb; 0.06 Cu; 0.025 Bi; 0.002 Ag; 0.001 Zn; 0.002 Fe
Beraloy	Wilbur B. Driver Co., Newark, N.J.	Cu; 1.9 Be; 0.5 max. Co; 0.5 max. Ni
Berylco 25	Beryllium Corp., Reading, Pa.	Cu; 1.9–2.15 Be; 0.05–0.4 Co; 0.1 max. Fe; 0.15 max. Si
Brass, aluminum	Generally available *	76 Cu; 22 Zn; 2 Al
Brass, cartridge	Generally available *	70 Cu; 30 Zn

Brass, forging	Scovill Mfg. Co., Waterbury, Conn.	60 Cu; 2 Pb; bal. Zn
Brass, free cutting	Scovill Mfg. Co., Waterbury, Conn.	61.5 Cu; 3 Pb; bal. Zn
Brass, high	Generally available *	66 Cu; 34 Zn
Brass, low	Generally available *	80 Cu; 20 Zn
Brass, low leaded	Scovill Mfg. Co., Waterbury, Conn.	67 Cu; 0.5 Pb; bal. Zn
Brass, med. leaded	Scovill Mfg. Co., Waterbury, Conn.	64.5 Cu; 1.0 Pb; bal. Zn
Brass, Naval	Generally available *	60 Cu; 39.25 Zn; 0.75 Sn
Brass, Naval, leaded	Scovill Mfg. Co., Waterbury, Conn.	60 Cu; 0.75 Sn; 1.75 Pb; bal. Zn
Brass, red	Generally available *	85 Cu; 15 Zn
Brass, tin	Scovill Mfg. Co., Waterbury, Conn.	92 Cu; 1 Sn; 7 Zn
Bronze, aluminum	Generally available *	82–95 Cu; 5–10 Al; Fe; Mn; Ni; Sn
Bronze, aluminum silicon	Bridgeport Brass Co., Bridgeport, Conn.	91 Cu; 7 Al; 2 Si
Bronze, commercial	Generally available *	90 Cu; 10 Zn
Bronze, commercial, leaded	Scovill Mfg. Co., Waterbury, Conn.	89 Cu; 1.75 Pb; 9.25 Zn
Bronze, 600 forgeable bearing	Mueller Brass Co., Port Huron, Mich.	
Bronze, gilding 95%	Scovill Mfg. Co., Waterbury, Conn.	95 Cu; 5 Zn
Bronze, hardware	Scovill Mfg. Co., Waterbury, Conn.	89 Cu; 8 Zn; 2 Pb; 1 Ni
Bronze, high-leaded tin	Mueller Brass Co., Port Huron, Mich.	
Bronze, manganese	Mueller Brass Co., Port Huron, Mich.	
Bronze, high-strength manganese	Mueller Brass Co., Port Huron, Mich.	
Bronze, phosphor, 5%	Generally available *	95 Cu; 5 Sn; P
Bronze, silicon, high	Bridgeport Brass Co., Bridgeport, Conn.	97 Cu; 3 Si
Bronze, silicon, low	Bridgeport Brass Co., Bridgeport, Conn.	98.2 Cu; 1.8 Si
Bronze, spring	Scovill Mfg. Co., Waterbury, Conn.	86.5 Cu; 2 Sn; 11.5 Zn
Bronze, Tobin	Generally available *	60 Cu; 39.25 Zn; 0.75 Sn
Buflokast gray iron	Buflovak Equipment Div., Blaw-Knox Co., Buffalo, N. Y.	Fe; 3.2–3.6 C; 2 max. Ni; 1–2 Si; 0.6–0.9 Mn
CA stainless	Cooper Alloy Fdry. Co., Hillside, N.J.	Various standard stainless steels
Calite A	Calorizing Co., Wilkinsburg, Pa.	Fe; 35 Ni; 15 Cr
Calite B28	Calorizing Co., Wilkinsburg, Pa.	Fe; 25 Cr; 10 Ni; 1 Mo
Carpenter stainless	Carpenter Steel Co., Reading, Pa.	Various standard stainless steels
Carpenter stainless 20	Carpenter Steel Co., Reading, Pa.	Fe; 29 Ni; 20 Cr; 3 Cu; 2 Mo; 0.07 max. C
Causul metal	Lunkenheimer Co., Cincinnati, Ohio	Fe; 19 Ni, 2.2–2.8 C; 4 Cu; 1.5 Cr
Chemalloy stainless	Electro-Alloys Div., Amer. Brake Shoe Co., Elyria, Ohio	Various standard stainless steels
Chemalloy A52N	Electro-Alloys Div., Amer. Brake Shoe Co., Elyria, Ohio	Fe; 21 Cr; 27 Ni; 2 Mo; 3 Cu; 2 Si
Chemalloy H1	Electro-Alloys Div., Amer. Brake Shoe Co., Elyria, Ohio	Ni; 21 Mo; 21 Fe
Chemalloy H2	Electro-Alloys Div., Amer. Brake Shoe Co., Elyria, Ohio	Ni; 29 Mo; 6 Fe
Chemalloy H3	Electro-Alloys Div., Amer. Brake Shoe Co., Elyria, Ohio	Ni; 14 Cr; 16 Mo; 4 W; 6 Fe
Chemalloy H4	Electro-Alloys Div., Amer. Brake Shoe Co., Elyria, Ohio	Ni; 10 Si; 3 Cu
Chlorimet 2	Duriron Co., Dayton, Ohio	63 Ni; 32 Mo; 3 Fe; 0.10 C; 1 Si

Materials	Manufacturer	Description
Chlorimet 3	Duriron Co., Dayton, Ohio	60 Ni; 18 Mo; 18 Cr; 3 Fe; 0.07 max. C; 1 Si
Chromax	Driver Harris Co., Harrison, N.J.	Fe; 19 Cr; 35 Ni
Chromel A	Hoskins Mfg. Co., Detroit, Mich.	80 Ni; 20 Cr
Chromel C and D	Hoskins Mfg. Co., Detroit, Mich.	35–61 Ni; 16–18.5 Cr; 23–46.5 Fe
Chromel P	Hoskins Mfg. Co., Detroit, Mich.	90 Ni; 10 Cr
Circle L stainless	Lebanon Steel Fdry., Lebanon, Pa.	Various standard stainless steels
Colonial 610	Vanadium Alloys Steel Co., Latrobe, Pa.	Fe; 16–18 Cr; 1 Ni; 0.12 max. C; S (optional)
Cooper stainless	Cooper Alloy Foundry Co., Hillside, N.J.	Various standard stainless steels
Cooper FA20	Cooper Alloy Foundry Co., Hillside, N.J.	28–30 Ni; 19–21 Cr; 3.5 Mo; 4–4.5 Cu; 1.5 max. Si; 0.07 max. C
Copel	Hoskins Mfg. Co., Detroit, Mich.	55 Cu; 45 Ni
Copper	Generally available *	99.9 + Cu
Copper, beryllium	Generally available *	97.5 Cu; 2.15 Be; 0.35 Ni
Copper, cadmium	Phelps Dodge Copper Prod. Corp., New York, N.Y.	99 Cu; 1 Cd
Copper, deoxidized	Generally available *	99.9 + Cu; 0.01–0.03 P
Copper, phosphorized	Mueller Brass Co., Port Huron, Mich.	99.9 Cu; trace P
Copper, tellurium	Chase Brass & Copper Co., Waterbury, Conn.	99.5 Cu; 0.5 Te
Corrosiron	Pacific Fdry. Co. Ltd., San Francisco, Calif.	Fe; 14.5 Si
Croloy intermediate	Babcock & Wilcox Tube Co., Beaver Falls, Pa.	Fe; 5, 7 or 9 Cr; 0.5 or 1 Mo
Croloy stainless	Babcock & Wilcox Tube Co., Beaver Falls, Pa.	Various standard stainless steels
Croloy clad plate	Babcock & Wilcox Co., New York, N.Y.	Steel clad with various standard stainless steels
Cupaloy	Westinghouse Electric Corp., Pittsburgh, Pa.	99.4 Cu; 0.1 Ag; 0.5 Cr
Cupron	Wilbur B. Driver Co., Newark, N.J.	Cu; 45 Ni
Cupro-Nickel, 15, 20, 30%	Generally available *	Cu; 15, 20 or 30 Ni
Disston stainless	Henry Disston & Sons Inc., Philadelphia, Pa.	Various standard stainless steels
Dopploy 30	Sowers Mfg. Co., Buffalo, N.Y.	Fe; 18.5 Ni; 2.35 Cr; 2.85 C; 1 Mn
Dowmetal	Dow Chemical Co., Midland, Mich.	Various magnesium alloys
Duraloy stainless	Duraloy Co., Scottdale, Pa.	Various standard stainless steels
Durco stainless	Duriron Co., Dayton, Ohio	Various standard stainless steels
Durco D-10	Duriron Co., Dayton, Ohio	56 Ni; 23 Cr; 8 Cu; 4 Mo; 2 W; 1 Mn
Durichlor	Duriron Co., Dayton, Ohio	Fe; 0.85 C; 14.5 Si; 3 Mo; 0.65 Mn
Durimet 20	Duriron Co., Dayton, Ohio	Fe; 20 Cr; 29 Ni; 0.07 max. C; 2 Mo; 4 Cu; 1 Si
Duriron	Duriron Co., Dayton, Ohio	Fe; 0.85 C; 14.5 Si; 0.65 Mn
Eastern stainless	Eastern Stainless Steel Corp., Baltimore, Md.	Various standard stainless steels
Enduro stainless	Republic Steel Corp., Cleveland, Ohio	Various standard stainless steels
Everdur 1000	Amer. Brass Co., Waterbury, Conn.	94.9 Cu; 4 Si; 1.1 Mn
Everdur 1010	Amer. Brass Co., Waterbury, Conn.	95.8 Cu; 3.1 Si; 1.1 Mn

Everdur 1015	Amer. Brass Co., Waterbury, Conn.	98.25 Cu; 1.5 Si; 0.25 Mn
Fahrite stainless	Ohio Steel Fdry. Co., Lima, Ohio	Various standard stainless steels
Fanweld	Fansteel Metallurgical Corp., North Chicago, Ill.	Hard facing rod; W, Cr, Co, TaC, CbC
Frontier 5	Frontier Bronze Corp., Niagara Falls, N.Y.	89 Cu; 10 Al; 1 Fe
Frontier 11	Frontier Bronze Corp., Niagara Falls, N.Y.	88 Cu; 5 Ni; 5 Sn; 2 Zn
Frontier 40	Frontier Bronze Corp., Niagara Falls, N.Y.	Cu; 5 Zn; 0.5 Mg; 0.5 Cr; 0.2 Ti
Gold	Baker & Co. Inc., Newark, N.J.	99.99 Au
Gun metal	Mueller Brass Co., Port Huron, Mich.	
Hastelloy A	Haynes Stellite Co., Kokomo, Ind.	Ni; 20–22 Mo; 18–20 Fe
Hastelloy B	Haynes Stellite Co., Kokomo, Ind.	Ni; 26–30 Mo; 4–7 Fe
Hastelloy C	Haynes Stellite Co., Kokomo, Ind.	Ni; 16–18 Mo; 4–7 Fe; 14–16 Cr; 3.75–5 W
Hastelloy D	Haynes Stellite Co., Kokomo, Ind.	Ni; 8–11 Si; 3–5 Cu
Haynes Stellite 1	Haynes Stellite Co., Kokomo, Ind.	Co; 30–32 Cr; 12–14 W
Haynes Stellite 6	Haynes Stellite Co., Kokomo, Ind.	Co; 27–29 Cr; 3.75–4.5 W
Haynes Stellite 12	Haynes Stellite Co., Kokomo, Ind.	Co; 28–30 Cr; 7.5–9 W
Haynes Stellite 98M2	Haynes Stellite Co., Kokomo, Ind.	Co; 30–31 Cr; 18.55–18.95 W; 3.5–3.75 Ni
Haynes Stellite Star J	Haynes Stellite Co., Kokomo, Ind.	Co; 32–32.75 Cr; 17.25–17.75 W
Herculoy	Revere Copper and Brass, New York, N.Y.	96–98 Cu; 1.5–3 Si; 0.25–1 Mn
Hytensl	Amer. Manganese Bronze Co., Philadelphia, Pa.	60–68 Cu; 20–24 Zn; 3–7 Al; 2.5–5 Mn; 2–4 Fe
Illium G	Burgess-Parr Co., Freeport, Ill.	56 Ni; 22.5 Cr; 6.5 Mo; 6.5 Fe; 6.5 Cu; Mn; Si; C
Inconel	International Nickel Co., New York, N.Y.	76 Ni; 15.5 Cr; 7.5 Fe; 0.08 C
Inconel-clad steel	Lukens Steel Co., Coatesville, Pa.	
Indium metal	Amer. Smelting and Ref. Co., New York, N.Y.	In
Ingersoll stainless	Ingersoll Steel Div., Borg-Warner Corp., Chicago, Ill.	Various standard stainless steels
Isocast 20	Empire Steel Castings, Inc., Reading, Pa.	Fe; 20 Cr; 29 Ni; 0.07 max. C; 3.5 min. Cu; 1.75 Mo; 1 min. Si
Isocast stainless	Empire Steel Castings, Inc., Reading, Pa.	Various standard stainless steels
Jessop stainless and stainless-clad	Jessop Steel Co., Washington, Pa.	Various standard stainless steels
K42B	Westinghouse Electric Corp., Pittsburgh, Pa.	42 Ni; 22 Co; 18 Cr; 14 Fe; 2.2 Ti
Kanthal alloys	C. O. Jelliff Mfg. Corp., Southport, Conn.	Fe; 20–25 Cr; Co; Al
Lead	Eagle-Picher Co., Cincinnati, Ohio	99.9 + Pb
Lead, antimonial	Amer. Smelting & Ref. Co., New York, N.Y.	94 Pb; 6 Sb
Lead, antimonial	Eagle-Picher Co., Cincinnati, Ohio	
Lead, antimonial	National Lead Co., New York, N.Y.	Pb; 6 Sb
Lead, antimonial	Northwest Lead Co., Seattle, Wash.	93.45 Pb; 6.5 Sb; 0.04–0.08 Cu
Lead, chemical	Eagle-Picher Co., Cincinnati, Ohio	
Lead, chemical	National Lead Co., New York, N.Y.	99.93 Pb; 0.06 Cu; 0.01 Ag; 0.005 Bi
Lead, chemical	Northwest Lead Co., Seattle, Wash.	99.95 Pb; 0.04–0.08 Cu
Lead, tellurium	Northwest Lead Co., Seattle, Wash.	99.9 Pb; 0.02–0.06 Te; 0.04–0.08 Cu
Lead, tellurium	Eagle-Picher Co., Cincinnati, Ohio	

Materials	Manufacturer	Description
Lead, tellurium	National Lead Co., New York, N.Y.	99.88 Pb; 0.04 Te; 0.06 Cu
Lukens clad steel	Lukens Steel Co., Coatesville, Pa.	Steel clad with Inconel, Monel, nickel or stainless
Michiana stainless	Michiana Products Corp., Michigan City, Ind.	Various standard stainless steels
Midvaloy stainless	Midvale Co., Philadelphia, Pa.	Various standard stainless steels
Milwaukee stainless	Milwaukee Steel Fdry., Milwaukee, Wis.	Various standard stainless steels
Misco stainless	Michigan Steel Casting Co., Detroit, Mich.	Various standard stainless steels
Misco 20	Michigan Steel Casting Co., Detroit, Mich.	Fe; 30 Ni; 20 Cr; 2.5 Mo; 4 Cu
Miscrome stainless	Michigan Steel Casting Co., Detroit, Mich.	Various standard stainless steels
Monel	International Nickel Co., New York, N.Y.	67 Ni; 30 Cu; 1.4 Fe; 0.15 C
Monel-clad	Lukens Steel Co., Coatesville, Pa.	
Mueller 85-5-5-5	Mueller Brass Co., Port Huron, Mich.	
Muntz metal	Generally available *	60 Cu; 40 Zn
N-3 metal	Lukenheimer Co., Cincinnati, Ohio	Cu; 32 Ni; 2.75 Pb; 9.5 Si; 0.75 Mn
National Al alloys	National Smelting Co., Cleveland, Ohio	Al; 0-4 Cu; 0-4 Mg; 0-7.5 Si; 0-0.6 Mn; 0-1.5 Ni
Niag	Mueller Brass Co., Port Huron, Mich.	
Nichrome	Driver Harris Co., Harrison, N.J.	60 Ni; 15 Cr; Fe
Nichrome V	Driver Harris Co., Newark, N.J.	80 Ni; 20 Cr
Nickel	International Nickel Co., New York, N.Y.	99.4 Ni; 0.05 C
Nickel L	International Nickel Co., New York, N.Y.	99.4 Ni; 0.01 C
Nickel-clad	Lukens Steel Co., Coatesville, Pa.	
Nickel silver, 5, 10, 18%	Generally available *	65 Cu; 5, 10 or 18 Ni; bal. Zn
Nicloy	Babcock & Wilcox Tube Co., Beaver Falls, Pa.	Fe; 3.5, 5 or 9 Ni
Ni-Hard	International Nickel Co., New York, N.Y.	Fe; 3.4 C; 1.5 Cr; 4.5 Ni; 0.6 Si
Nilstain	Wilbur B. Driver Co., Newark, N.J.	Fe; 18-20 Cr; 8-10 Ni; 0.2 max. C; 2 max. Mn
Ni-Resist	International Nickel Co., New York, N.Y.	Fe; 2.8 C; 14 or 20 Ni; 6 Cu (optional); 2 Cr; 2 Si
Nirex	Driver Harris Co., Harrison, N.J.	80 Ni; 14 Cr; 6 Fe
NS-5 metal	Lunkenheimer Co., Cincinnati, Ohio	50 Ni; 46 Cu; 2.2 Si; 1.9 Mn
Olympic bronze, Type A	Chase Brass & Copper Co., Waterbury, Conn.	96 Cu; 3 Si; 1 Zn
Palladium	Baker & Co., Newark, N.J.	99.99 Pd
Pennalloy	Pennsylvania Elec. Steel Casting Co., Hamburg, Pa.	
Permite Al alloys	Aluminum Industries, Cincinnati, Ohio	Al; 0-5 Cu; 1.5-7.5 Si; 0-1 Fe; 0-0.4 Mg
Pioneer	Pioneer Alloy Products Co., Cleveland, Ohio	65 Ni; Cr; Mo; Fe
Platinum	Baker & Co., Newark, N.J.	99.99 Pt
Platinum	J. Bishop & Co., Malvern, Pa.	99.95 Pt
Platinum, iridio	Baker & Co., Newark, N.J.	Pt; 5-30 Ir
Platinum, iridium	J. Bishop & Co., Malvern, Pa.	Pt; 10-30 Ir

Platinum, rhodio	Baker & Co., Newark, N.J.	Pt; 5–40 Rh
Pyrasteel	Chicago Steel Fdry. Co., Chicago, Ill.	Fe; 25–27 Cr; 12–14 Ni; 0.1–0.35 C; Mo, Cb, Se (optional)
Pyrocast	Pacific Fdry. Co. Ltd., San Francisco, Calif.	Fe; 25 Cr
Pyrocast stainless	Pacific Fdry. Co. Ltd., San Francisco, Calif.	Various standard stainless steels
Refractaloy 26	Westinghouse Electric Corp., Pittsburgh, Pa.	37 Ni; 20 Co; 18 Cr; 3 Mo; 2.8 Ti; 18 Fe
Refractaloy 70	Westinghouse Electric Corp., Pittsburgh, Pa.	20 Ni; 30 Co; 20 Cr; 15 Fe; 8 Mo; 4 W; 2 Mn
Resistac	Amer. Manganese Bronze Co., Philadelphia, Pa.	90 Cu; 10 Al
Revalon	Revere Copper and Brass, New York, N.Y.	76 Cu; 22 Zn; 2 Al
Rex Z-metal	Chain Belt Co., Milwaukee, Wis.	Iron carbide particles in ferrite matrix
Reynolds 2S	Reynolds Metals Co., Louisville, Ky.	99 Al; 1 max. Fe + Si; 0.2 max. Cu
Reynolds 3S	Reynolds Metals Co., Louisville, Ky.	Al; 1–1.5 Mn; 0.7 max. Fe; 0.6 max. Si; 0.2 Cu
Reynolds 14S	Reynolds Metals Co., Louisville, Ky.	Al; 3.9–5 Cu; 0.5–1.2 Si; 1 max. Fe; 0.4–1.2 Mn; 0.2–0.8 Mg
Reynolds 17S	Reynolds Metals Co., Louisville, Ky.	Al; 3.5–4.5 Cu; 0.8 max. Si; 1 max. Fe; 0.4–1 Mn; 0.2–0.8 Mg
Reynolds 18S	Reynolds Metals Co., Louisville, Ky.	Al; 3.5–4.5 Cu; 1.7–2.3 Ni; 0.9 max. Si; 1 max. Fe; 0.45–0.9 Mg
Reynolds 24S	Reynolds Metals Co., Louisville, Ky.	Al; 3.8–4.9 Cu; 1.2–1.8 Mg; 0.5 max. Si
Reynolds 24S Pureclad	Reynolds Metals Co., Louisville, Ky.	Al 24S core covered with Al of high purity
Reynolds 25S	Reynolds Metals Co., Louisville, Ky.	Al; 3.9–5 Cu; 0.5–1.2 Si; 1 max. Fe
Reynolds 32S	Reynolds Metals Co., Louisville, Ky.	Al; 11–13.5 Si; 0.5–1.3 Cu; 1.0 max. Fe; 0.8–1.3 Mg; 0.5–1.3 Ni
Reynolds A51S	Reynolds Metals Co., Louisville, Ky.	Al; 0.6–1.2 Si; 1 max. Fe; 0.35 Cu; 0.45–0.8 Mg
Reynolds 52S	Reynolds Metals Co., Louisville, Ky.	Al; 2.2–2.8 Mg; 0.45 max. Fe plus Si; 0.1 max. Cu
Reynolds 53S	Reynolds Metals Co., Louisville, Ky.	Al; 0.35 max. Fe; 1.1–1.4 Mg; 0.15–0.35 Cr
Reynolds 61S	Reynolds Metals Co., Louisville, Ky.	Al; 0.4–0.8 Si; 0.7 max. Fe; 0.8–1.2 Mg
Reynolds R301	Reynolds Metals Co., Louisville, Ky.	High-strength Al alloy core clad with corrosion-resistant Al alloy of intermediate strength
Rezistal stainless	Crucible Steel Co. of Amer., New York, N.Y.	Various standard stainless steels
Roofloy	Amer. Smelting & Ref. Co., New York, N.Y.	Pb; 0.25 Sn; 0.02 Mg; 0.02 Bi
St. Joe lead	St. Joseph Lead Co., New York, N.Y.	99.90 + Pb; 0.04–0.08 Cu; 0.002–0.02 Ag; 0.002 max. Fe; 0.001 max. Zn; 0.002 max. As, Sb, Sn
Silver	Baker & Co. Inc., Newark, N.J.	99.9 + Ag
Silver	Handy & Harman, New York, N.Y.	99.9 + Ag
Stainless-clad 304	Lukens Steel Co., Coatesville, Pa.	
Stainless-clad 316	Lukens Steel Co., Coatesville, Pa.	
Stainless-clad 347	Lukens Steel Co., Coatesville, Pa.	
Stainless-clad 410	Lukens Steel Co., Coatesville, Pa.	
Stainless-clad 430	Lukens Steel Co., Coatesville, Pa.	
Stainless Type 301	NOTE: Listed below are the producers of standard stainless steels for which type analyses have been established by the American Iron and Steel Institute	Fe; 16–18 Cr; 6–8 Ni; 0.08–0.15 C
Stainless Type 302		Fe; 17–19 Cr; 8–10 Ni; 0.08–0.15 C
Stainless Type 302B		Fe; 17–19 Cr; 8–10 Ni; 0.08–0.15 C; 2–3 Si

Materials	Manufacturer	Description
Stainless Type 303	Allegheny Ludlum Steel Corp., Pittsburgh, Pa. Alloy Metal Wire Co., Prospect Park, Pa. Amer. Chain & Cable Co., Bridgeport, Conn. Amer. Rolling Mill Co., Middletown, Ohio Babcock & Wilcox Tube Co., Beaver Falls, Pa. Bethlehem Steel Co., Bethlehem, Pa. A. M. Byers Co., Pittsburgh, Pa. Carnegie-Illinois Steel Co., Pittsburgh, Pa. Carpenter Steel Co., Reading, Pa. Cooper Alloy Fdry. Co., Elizabeth, N.J. Copperweld Steel Co., Warren, Ohio Crucible Steel Co. of America, New York, N.Y. Wilbur B. Driver Co., Newark, N.J. Eastern Stainless Steel Corp., Baltimore, Md. Firth Sterling Steel Co., McKeesport, Pa. Globe Steel Tubes Co., Milwaukee, Wis. Henry Disston & Sons, Philadelphia, Pa. Ingersoll Steel Div., Borg-Warner Corp., New Castle, Ind. Jessop Steel Co., Washington, Pa. Joslyn Mfg. & Supply Co., Chicago, Ill. Latrobe Electric Steel Co., Latrobe, Pa. McLouth Steel Corp., Detroit, Mich. Michiana Products Corp., Michigan City, Ind. Midvale Co., Philadelphia, Pa. Pittsburgh Steel Co., Pittsburgh, Pa. Timken Roller Bearing Co., Canton, Ohio Republic Steel Corp., Cleveland, Ohio Rotary Electric Steel Corp., Detroit, Mich. Sharon Steel Corp., Sharon, Pa. Stanley Works, New Britain, Conn. Summerill Tubing Co., Bridgeport, Pa. Superior Steel Corp., Carnegie, Pa. Trent Tube Mfg. Co., East Troy, Wis. Universal Cyclops Steel Corp., Bridgeville, Pa. Vanadium Alloys Steel Co., Latrobe, Pa. Wallingford Steel Co., Wallingford, Conn.	Fe; 17–19 Cr; 8–10 Ni; 0.15 max. C; 0.07 min. P, S, Se; 0.6 max. Zr, Mo; 2 max. Mn
Stainless Type 304		Fe; 18–20 Cr; 8–11 Ni; 0.08 max. C; 2 max. Mn
Stainless Type 308		Fe; 19–21 Cr; 10–12 Ni; 0.08 max. C
Stainless Type 309		Fe; 22–24 Cr; 12–15 Ni; 0.2 max. C
Stainless Type 310		Fe; 24–26 Cr; 19–22 Ni; 0.25 max. C
Stainless Type 316		Fe; 16–18 Cr; 10–14 Ni; 0.1 max. C; 1.75–2.75 Mo
Stainless Type 317		Fe; 17.5–20 Cr; 10–14 Ni; 0.1 max. C; 3–4 Mo
Stainless Type 321		Fe; 17–19 Cr; 8–11 Ni; Ti, 5xC min.
Stainless Type 347		Fe; 17–19 Cr; 9–12 Ni; Cb, 10xC min.
Stainless Type 403		Fe; 11.5–13 Cr; 0.15 max. C (turbine quality)
Stainless Type 405		Fe; 11.5–13.5 Cr; 0.08 max. C; 0.1–0.3 Al
Stainless Type 406		Fe; 12–14 Cr; 0.15 max. C; 3.5–4.5 Al
Stainless Type 410		Fe; 11.5–13.5 Cr; 0.15 max. C
Stainless Type 414		Fe; 11.5–13.5 Cr; 1.25–2.5 Ni; 0.15 max. C
Stainless Type 416		Fe; 12–14 Cr; 0.15 max. C; 0.07 min. P, S, Se; 0.6 max. Zr, Mo
Stainless Type 418		Fe; 12–14 Cr; 0.15 max. C; 2.5–3.5 W
Stainless Type 420		Fe; 12–14 Cr; 0.15 min. C
Stainless Type 430		Fe; 14–18 Cr; 0.12 max. C
Stainless Type 430F		Fe; 14–18 Cr; 0.12 max. C; 0.07 min. P, S, Se; 0.6 max. Zr, Mo
Stainless Type 431		Fe; 15–17 Cr; 1.25–2.5 Ni; 0.2 max. C
Stainless Type 440A		Fe; 16–18 Cr; 0.6–0.75 C; 0.75 max. Mo
Stainless Type 440B		Fe; 16–18 Cr; 0.75–0.95 C; 0.75 max. Mo
Stainless Type 440C		Fe; 16–18 Cr; 0.95–1.2 C; 0.75 max. Mo
Stainless Type 442		Fe; 18–23 Cr; 0.25 max. C
Stainless Type 443		Fe; 18–23 Cr; 0.2 max. C; 0.9–1.25 Cu
Stainless Type 446		Fe; 23–27 Cr; 0.35 max. C; 0.25 max. N
Stainless Type 501		Fe; 4–6 Cr; 0.1 min. C
Stainless Type 502		Fe; 4–6 Cr; 0.1 max. C
Stainless Type CA-15		Fe; 11–14 Cr; 1 max. Ni; 0.15 max. C
Stainless Type CA-40		Fe; 11–14 Cr; 1 max. Ni; 0.2–0.4 C
Stainless Type CB-30		Fe; 18–22 Cr; 2 max. Ni; 0.3 max. C
Stainless Type CC-35		Fe; 26–30 Cr; 4 max. Ni; 0.35 max. C
Stainless Type CC-50		Fe; 26–30 Cr; 4 max. Ni; 0.5 max. C
Stainless Type CD-10M		Fe; 27–30 Cr; 3–6 Ni; 0.1 max. C; 2 max. Mo

Stainless Type CE-30	NOTE: Listed below are the producers of standard cast stainless steel for which type analyses have been established by the Alloy Casting Institute. Allegheny Ludlum Steel Corp., Pittsburgh, Pa. Amer. Cast Iron Pipe Co., Birmingham, Ala. American Manganese Steel Div., American Brake Shoe & Fdry. Co., Chicago Heights, Ill. American Steel Castings Co., Newark, N.J. Atlas Fdry. Co., Irvington, N.J. Babcock & Wilcox Co., Barberton, Ohio Calorizing Co., Wilkinsburg, Pa. Chicago Steel Fdry., Chicago, Ill. Cooper Alloy Fdry. Co., Elizabeth, N.J. Crane Co., Chicago, Ill. Driver Harris Co., Harrison, N.J. Duraloy Co., Scottdale, Pa. Duriron Co., Inc., Dayton, Ohio Electric Steel Fdry. Co., Portland, Ore. Electro-Alloys Div., Amer. Brake Shoe Co., Elyria, Ohio Empire Steel Castings, Inc., Reading, Pa. General Alloys Co., Boston, Mass. General Metals Corp., Oakland, Calif. Grede Foundries, Milwaukee, Wis. Haynes Stellite Co., Kokomo, Ind. Hoskins Mfg. Co., Detroit, Mich. Key Co., East St. Louis, Ill. Lebanon Steel Fdry., Lebanon, Pa. Michiana Products Corp., Michigan City, Ind. Michigan Steel Casting Co., Detroit, Mich. Midvale Co., Philadelphia, Pa. Milwaukee Steel Fdry., Milwaukee, Wis. National Alloy Div., Blaw-Knox Co., Blawknox, Pa. Ohio Steel Fdry. Co., Cincinnati, Ohio Otis Elevator Co., Buffalo, N.Y. Pacific Fdry. Co., Ltd., San Francisco, Calif. Shawinigan Chemicals, Ltd., Montreal, Que. Sivyer Steel Casting Co., Milwaukee, Wis. Standard Alloy Co., Cleveland, Ohio	Fe; 26-30 Cr; 8-11 Ni; 0.3 max. C
Stainless Type CF-7		Fe; 18-20 Cr; 8-10 Ni; 0.07 max. C
Stainless Type CF-10		Fe; 18-20 Cr; 8-10 Ni; 0.1 max. C
Stainless Type CF-16		Fe; 18-20 Cr; 8-10 Ni; 0.16 max. C
Stainless Type CF-20		Fe; 18-20 Cr; 8-10 Ni; 0.2 max. C
Stainless Type CF-7Se		Fe; 18-20 Cr; 8-10 Ni; 0.07 max. C; 0.2-0.35 Se
Stainless Type CF-7C		Fe; 18-20 Cr; 8-10 Ni; 0.07 max. C; 8xC-1 Cb
Stainless Type CF-7M		Fe; 18-20 Cr; 8-10 Ni; 0.07 max. C; 1.5-3.5 Mo
Stainless Type CF-10M		Fe; 18-20 Cr; 8-10 Ni; 0.1 max. C; 1.5-3.5 Mo
Stainless Type CF-16M		Fe; 18-20 Cr; 8-10 Ni; 0.16 max. C; 1.5-3.5 Mo
Stainless Type CF-7MC		Fe; 18-20 Cr; 8-10 Ni; 0.07 max. C; 1.5-3.5 Mo; 8xC-1 Cb
Stainless Type CG-7		Fe; 20-22 Cr; 10-12 Ni; 0.07 max. C
Stainless Type CG-10		Fe; 20-22 Cr; 10-12 Ni; 0.1 max. C
Stainless Type CG-16		Fe; 20-22 Cr; 10-12 Ni; 0.16 max. C
Stainless Type CG-16 Se		Fe; 20-22 Cr; 10-12 Ni; 0.16 max. C; 0.2-0.35 Se
Stainless Type CG-7C		Fe; 20-22 Cr; 10-12 Ni; 0.07 max. C; 8xC-1 Cb
Stainless Type CG-7M		Fe; 20-22 Cr; 10-12 Ni; 0.07 max. C; 1.5-3.5 Mo
Stainless Type CG-10M		Fe; 20-22 Cr; 10-12 Ni; 0.1 max. C; 1.5-3.5 Mo
Stainless Type CG-16M		Fe; 20-22 Cr; 10-12 Ni; 0.16 max. C; 1.5-3.5 Mo
Stainless Type CG-7MC		Fe; 20-22 Cr; 10-12 Ni; 0.07 max. C; 1.5-3.5 Mo; 8xC-1 Cb
Stainless Type CH-10		Fe; 22-26 Cr; 12-15 Ni; 0.1 max. C
Stainless Type CH-20		Fe; 22-26 Cr; 12-15 Ni; 0.2 max. C
Stainless Type CH-10C		Fe; 22-26 Cr; 12-15 Ni; 0.1 max. C; 8xC-1 Cb
Stainless Type CH-10M		Fe; 22-26 Cr; 12-15 Ni; 0.1 max. C; 1.5-3.5 Mo
Stainless Type CH-20M		Fe; 22-26 Cr; 12-15 Ni; 0.2 max. C; 1.5-3.5 Mo
Stainless Type CH-10MC		Fe; 22-26 Cr; 12-15 Ni; 0.1 max. C; 1.5-3.5 Mo; 8xC-1 Cb
Stainless Type CK-25		Fe; 23-27 Cr; 19-22 Ni; 0.25 max. C
Stainless Type CM-25		Fe; 8-11 Cr; 19-22 Ni; 0.25 max. C
Stainless Type CN-7		Fe; 18-22 Cr; 20-30 Ni; 0.07 max. C; may contain others
Stainless Type CN-25		Fe; 18-22 Cr; 20-30 Ni; 0.25 max. C; may contain others
Stainless Type CS-25		Fe; 8-12 Cr; 29-32 Ni; 0.25 max. C
Stainless Type CT-7		Fe; 13-17 Cr; 34-37 Ni; 0.07 max. C; may contain others
Stainless Type CT-25		Fe; 13-17 Cr; 34-37 Ni; 0.25 max. C; may contain others
Stainless Type HB		Fe; 18-22 Cr; 2 max. Ni
Stainless Type HC		Fe; 26-30 Cr; 4 max. Ni
Stainless Type HD		Fe; 26-30 Cr; 3-6 Ni
Stainless Type HE		Fe; 26-30 Cr; 8-11 Ni
Stainless Type HF		Fe; 18-23 Cr; 8-11 Ni
Stainless Type HH		Fe; 23-27 Cr; 11-14 Ni

Materials	Manufacturer	Description
Stainless Type HI	Sterling Alloys Inc., Woburn, Mass. Symington-Gould Corp., Rochester, N.Y. Taylor Wharton Iron & Steel Co., High Bridge, N.J. Utility Electric Steel Fdry., Los Angeles, Calif. Warman Steel Casting Co., Huntington Park, Calif.	Fe; 26–30 Cr; 14–17 Ni
Stainless Type HK		Fe; 23–27 Cr; 19–22 Ni
Stainless Type HL		Fe; 28–32 Cr; 19–22 Ni
Stainless Type HN		Fe; 18–22 Cr; 23–26 Ni
Stainless Type HP		Fe; 28–32 Cr; 29–31 Ni
Stainless Type HS		Fe; 8–12 Cr; 29–32 Ni
Stainless Type HT		Fe; 13–17 Cr; 33–37 Ni
Stainless Type HU		Fe; 17–21 Cr; 37–41 Ni
Stainless Type HW		Fe; 10–14 Cr; 58–62 Ni
Stainless Type HX		Fe; 15–19 Cr; 64–68 Ni
Still metal	Amer. Manganese Bronze Co., Philadelphia, Pa.	
Stoody 1	Stoody Co., Whittier, Calif.	Nonferrous; Co, Cr, W welding rod
Stoody 6	Stoody Co., Whittier, Calif.	Nonferrous; Co, Cr, W welding rod
Super nickel	Amer. Brass Co., Waterbury, Conn.	70 Cu; 30 Ni
Tantalum	Fansteel Metallurgical Corp., North Chicago, Ill.	99.9 + Ta
Telnic bronze	Chase Brass and Copper Co., Waterbury, Conn.	98.3 Cu; 1 Ni; 0.2 P; 0.5 Te
Thermalloy stainless	Electro-Alloys Div., Amer. Brake Shoe Co., Elyria, Ohio	Various standard heat-resistant stainless steels
Tisco 150 alloy	Taylor-Wharton Iron and Steel Co., Easton, Pa.	
Tisco timang Mn Ni steel	Taylor-Wharton Iron and Steel Co., Easton, Pa.	
Tisco Mn steel	Taylor-Wharton Iron and Steel Co., Easton, Pa.	Fe; 12 Mn (Hadfield type)
Toncan Cu Mo iron	Republic Steel Corp., Cleveland, Ohio	
Tophet A	Wilbur B. Driver Co., Newark, N.J.	80 Ni; 20 Cr
Tophet C	Wilbur B. Driver Co., Newark, N.J.	Fe; 60 Ni; 15 Cr
Tophet D	Wilbur B. Driver Co., Newark, N.J.	Fe; 35 Ni; 18.5 Cr
Tri-Clover	Tri-Clover Machine Co., Kenosha, Wis.	Various standard stainless-steel fittings
Tube borium	Stoody Co., Whittier, Calif.	
Tuf-Stuf	Mueller Brass Co., Port Huron, Mich.	86.9 Cu; 10 Al; 3 Fe; 0.1 Mn
U.S.S. stainless	Carnegie-Illinois Steel Corp., Pittsburgh, Pa.	Various standard stainless steels
Utiloy stainless	Utility Electric Steel Fdry., Los Angeles, Calif.	Various standard stainless steels
Utiloy 20	Utility Electric Steel Fdry., Los Angeles, Calif.	20 Cr; 29 Ni; 1.75 Mo; 0.07 max. C
Utiloy 100	Utility Electric Steel Fdry., Los Angeles, Calif.	98 Ni; 1 Si; 0.25 C
Utiloy H	Utility Electric Steel Fdry., Los Angeles, Calif.	22–26 Cr; 11–13 Ni; 0.3 C
Utiloy NH	Utility Electric Steel Fdry., Los Angeles, Calif.	14–17 Cr; 34–37 Ni; 0.2–0.6 C
Vanadium stainless	Vanadium Alloys Steel Co., Latrobe, Pa.	Various standard stainless steels
Worthite	Worthington Pump and Machinery Corp., Harrison, N.J.	Fe; 20 Cr; 24 Ni; 0.07 max. C; 3.25 Si; 3 Mo; 1.75 Cu; 0.6 Mn

Wrought iron	A. M. Byers Co., Pittsburgh, Pa.	Fe; 0.03 max. C; 0.05 max. Mn; 0.10–0.12 P; 0.025 max. S; 0.10–0.15 Si; 2.5–3.0 slag
Wyndaloy	Wyndale Mfg. Corp., Indianapolis, Ind.	
	Carbon and graphite	
Impervite	General Ceramics and Steatite Corp., Keasbey, N.J.	Resin-impregnated graphite. Mostly for heat exchangers
International	International Graphite and Electrode Corp., St. Marys, Pa.	Graphite. Electrodes and various shapes
Karbate (carbon)	National Carbon Co., Cleveland, Ohio	Impervious carbon Pipe, fittings, valves, pumps, heat exchangers, towers and auxiliary parts, tanks, brick, plates, tubes, special shapes, seal rings, injection parts
Karbate (graphite)	National Carbon Co., Cleveland, Ohio	Impervious graphite
Kempruf carbon brick	Electro Chemical Supply and Engineering Co., Paoli, Pa.	Dense carbonaceous material
National Kempruf	National Carbon Co., Cleveland, Ohio	Carbon Brick, plates, tubes, cylinders, beams, raschig rings, pipe, fittings, towers and auxiliary parts, molds, bushings, special shapes
National Acheson	National Carbon Co., Cleveland, Ohio	Graphite
Speer	Speer Carbon Co., St. Marys, Pa	Carbon and graphite. Brick, plates, blocks, tubes, cylinders, bushings, shapes
Stackpole	Stackpole Carbon Co., St. Marys, Pa.	Carbon and graphite. Tubes, pipe, rods, plates, bearings, seal rings, crucibles, heat-treating boxes and molds
Stackpole	Stackpole Carbon Co., St. Marys, Pa.	Impervious graphite. Pipe, bearings, seal rings, special shapes (*injector body and nozzles*)
	Cement, mortar, putty	
Acichlor	Pecora Paint Co., Philadelphia, Pa.	Firm putty
Acidol	The Sullivan Co., Memphis, Tenn.	Pouring cements
Acitite	Pecora Paint Co., Philadelphia, Pa.	Ready-mixed cement; troweling
Alk-Li-Pruf	Electro Chemical Supply and Engineering Co., Paoli, Pa.	Alkali-resistant, synthetic-type cement
Alkor	Atlas Mineral Products Co., Mertztown, Pa.	Furan derivative; carbon aggregate
Asplit	Pennsylvania Salt Mfg. Co., Philadelphia, Pa.	Self-hardening resin cement
Basolit, carbon	Nukem Products Corp., Buffalo, N.Y.	Carbon-sulphur cement
Basolit, standard	Nukem Products Corp., Buffalo, N.Y.	Sulphur silicate-based cement
Brimsto	Electro Chemical Supply and Engineering Co., Paoli, Pa.	Sulphur-base, hard-setting, smooth-surfaced cement
Carbo-Fix	Carboline Co., St. Louis, Mo.	(Carbon) Room temperature, thermosetting carbon cements
Carbo-Flex		
Carbo-Insulate		
Carbo-Mold		

Materials	Manufacturer	Description
Carbo-Korez	Atlas Mineral Products Co., Mertztown, Pa.	Phenol-formaldehyde; carbon aggregate
Carbo Vitrobond	Atlas Mineral Products Co., Mertztown, Pa.	Sulphur-Thiokol cement
Carolina	Charlotte Chemical Laboratories, Charlotte, N.C.	Acidproof cement
Causplit	Pennsylvania Salt Mfg. Co., Philadelphia, Pa.	Self-hardening resin cement
Ceilcote resin cement	Ceilcote Co., Cleveland, Ohio	Furan resin cement with silica and carbon fillers
Charlab	Charlotte Chemical Laboratories, Charlotte, N.C.	Chemical putty
Chemstone	Johns-Manville Sales Corp., New York, N.Y.	Pressed sheets made from asbestos, cement and inert mineral filler
Compo-Bond	Ceilcote Co., Cleveland, Ohio	Silicate bonding cement, liquid and powder
Duralon	U.S. Stoneware Co., Akron, Ohio	Furan-base resin cements
Durasite	U.S. Stoneware Co., Akron, Ohio	Furan-base resin cements
Duro standard	Electro Chemical Supply and Engineering Co., Paoli, Pa.	Hard, dense, silicate-type cement
Duro XXX(triplex)	Electro Chemical Supply and Engineering Co., Paoli, Pa.	Exceedingly dense, silicate-type cement
Filtros	Filtros Inc., East Rochester, N.Y.	Acidproof cement
Kemo paste	Electro Chemical Supply and Engineering Co., Paoli, Pa.	Mineral-type filler for portland cement. (Makes it appreciably acid resistant)
Korez	Atlas Mineral Products Co., Mertztown, Pa.	Phenol-formaldehyde; silica aggregate
Lumnite	Lumnite Div., Universal Atlas Cement Co., New York, N.Y.	Hydraulic cement; powder for mixing with aggregate and water to make concrete
N-380 silicate	Philadelphia Quartz Co., Philadelphia, Pa.	Sodium silicate; to be combined with special proprietary quick-setting cements at time of use
N-series	Union Bay State Chemical Co., Cambridge, Mass.	Neoprene-base cements
Nu mastic	Nukem Products Corp., Buffalo, N.Y.	Asphalt base, high-temperature cement
Nukem all-purpose	Nukem Products Corp., Buffalo, N.Y.	Resinous cement; chemical setting
Nukem silicate	Nukem Products Corp., Buffalo, N.Y.	Silicate cement
Pecomastic	Pecora Paint Co., Philadelphia, Pa.	Putty; troweling; brushing
Penchlor acidproof	Pennsylvania Salt Mfg. Co., Philadelphia, Pa.	Chemical setting silicate cement
Penchlor acidproof S25	Pennsylvania Salt Mfg. Co., Philadelphia, Pa.	Chemical setting silicate cement
Penchlor acidproof, Pfaudler grade	Pennsylvania Salt Mfg. Co., Philadelphia, Pa.	Chemical setting, low porosity silicate cement
Penchlor fireproof	Pennsylvania Salt Mfg. Co., Philadelphia, Pa.	Chemical setting silicate cement
Pennsalt HF and HFK	Pennsylvania Salt Mfg. Co., Philadelphia, Pa.	Self-hardening resin cement
Pennsalt PRF and PRFK	Pennsylvania Salt Mfg. Co., Philadelphia, Pa.	Self-hardening resin cement
Permanite	Maurice A. Knight, Akron, Ohio	Furane base resin cement
Plastite	U.S. Stoneware Co., Akron, Ohio	Caulking putty
Plasul Basolit	Nukem Products Corp., Buffalo, N.Y.	Plasticized sulphur-silicate cement
Porox	Patterson Fdry. & Machine Co., East Liverpool, Ohio	Silicate cement
Quigley	Quigley Co., New York, N.Y.	Acidproof cements

Reardon	Reardon Industries, Cincinnati, Ohio	Acidproof cement
Redux	Resinous Products & Chemicals Co., Philadelphia, Pa.	Metal-to-metal resin adhesive
Sauereisen 31	Sauereisen Cement Co., Pittsburgh, Pa.	Acidproof cement. Sodium silicate base
Sauereisen 44	Sauereisen Cement Co., Pittsburgh, Pa.	Acid tank sealer. Nonhardening bituminous-base plastic
Sauereisen 46	Sauereisen Cement Co., Pittsburgh, Pa.	Hydrofluoric acid cement. Zirconium-base melting compound
Sauereisen 48	Sauereisen Cement Co., Pittsburgh, Pa.	Joint compound. Sulphur-base melting compound
Sauereisen 49	Sauereisen Cement Co., Pittsburgh, Pa.	Resin-base melting compound
Sealtex	Nukem Products Corp., Buffalo, N.Y.	Cold-setting rubberized asphaltic compound
S special silicate	Philadelphia Quartz Co., Philadelphia, Pa.	Low-alkaline silicate for use with silica cements
Stackpole	Stackpole Carbon Co., St. Marys, Pa.	Carbonaceous cements for carbon, graphite, and carbon-to-metal joints
Staminite	Robinson Clay Product Co., Akron, Ohio	Acidproof cement
Sulsilo	The Sullivan Co., Memphis, Tenn.	Pre-mixed silicate cement
Syntho	Electro Chemical Supply and Engineering Co., Paoli, Pa.	Dense, impervious, synthetic-type cement
Thiokol	Thiokol Corp., Trenton, N.J.	Liquid (100% solids) rubber polymers
Transite	Johns-Manville Sales Corp., New York, N.Y.	Asbestos fiber and cement combined under pressure. Pipe, flat, and corrugated sheet
Vitrex	Atlas Mineral Products Co., Mertztown, Pa.	Sodium silicate; sets by chemical reaction
Vitrobond	Atlas Mineral Products Co., Mertztown, Pa.	Sulphur-Thiokol cement

Ceramics

Aco	Custodis Construction Co., New York, N.Y.	Acidproof brick and packing rings
Alsop glass lining	Alsop Engineering Co., Milldale, Conn.	Glass-lined tanks, mixers, and filters
Amersil fused silica	Amersil Co., Inc., Hillside, N.J.	Fused silica ware. Pans, pipes, gas coolers, absorbers, insulators, tubes, plates
Carrara	Pittsburgh Plate Glass Co., Pittsburgh, Pa.	Structural glass, flat or bent
Ceratherm	U.S. Stoneware Co., Akron, Ohio	Ceramic ware. Process equipment
Ceraware	General Ceramics and Steatite Corp., Keasbey, N.J.	Chemical stoneware. Towers, tanks, pumps, etc.
Cerawite	General Ceramics and Steatite Corp., Keasbey, N.J.	Chemical porcelain. Piping, valves, etc.
Duro	Electro Chemical Supply and Engineering Co., Paoli, Pa.	Vitreous, acidproof brick
Fiberglas	Owens-Corning Fiberglas Corp., Toledo, Ohio	Fibrous glass cloth and mat. Air filters, thermal insulation, tower packing, filter cloth
Glascote	Glascote Products, Inc., Cleveland, Ohio	Borosilicate glass lining fused to steel
Hanovia fused quartz	Hanovia Chemical & Mfg. Co., Newark, N.J.	Transparent fused quartz in all shapes
Illinois	Illinois Electric Porcelain Co., Macomb, Ill.	Ceramic chemical porcelain. Pipe, valves, fittings
Knightware	Maurice A. Knight, Akron, Ohio	Chemical stoneware, Tanks, kettles, pipe, fittings, valves, pumps, coils, filters, etc.

Materials	Manufacturer	Description
Lapp porcelain	Lapp Insulator Co., Le Roy, N.Y.	Chemical porcelain. Pipe, fittings, valves, tower packing, special shapes
Locke porcelain	Locke Inc., Baltimore, Md.	Chemical porcelain. Balls for ball mills, brick, piping, valves, containers
Pennvernon	Pittsburgh Plate Glass Co., Pittsburgh, Pa.	Window glass, flat
Permaglas	A. O. Smith Corp., Milwaukee, Wis.	Glass-lined steel equipment
Pfaudler	The Pfaudler Co., Rochester, N.Y.	Glass-lined steel equipment. Tanks, pipe, fittings, valves
Pittsburgh plate glass	Pittsburgh Plate Glass Co., Pittsburgh, Pa.	Polished plate glass, flat or bent
Pyrex	Corning Glass Works, Corning, N.Y.	Glass. Pipe, fittings, sight glasses, gage glasses, heat-resistant plate
"U.S." chemical stoneware	U.S. Stoneware Co., Akron, Ohio	Chemical stoneware. Tanks, kettles, pipe, fittings, valves, pumps, coils, filters, etc.
Vitreo	Vitreous Steel Products Co., Cleveland, Ohio	Porcelain enamel drying trays
Vitreosil	The Thermal Syndicate Ltd., New York, N.Y.	Vitreous silica, approx. 99.8% silica; pipes and vessels up to 50-gal. capacity; 30 in. diameter, 10 ft. length
Vitreous enamel	Vitreous Enameling & Stamping Co., New York, N.Y.	Enameled tanks and specialties
Vycor	Corning Glass Works, Corning, N.Y.	96% Silica glass. Tubing, rods, flat ware, various shapes
	Plastics	
Ace Saran	Amer. Hard Rubber Co., Butler, N.J.	Vinylidene chloride. Pipe, fittings, tubing
Ace Parian	Amer. Hard Rubber Co., Butler, N.J.	Polyethylene. Pipe, fittings, tubing
Catalin	Catalin Corp. of Amer., New York, N.Y.	Cast phenol-formaldehyde resin
Ceilcote	Ceilcote Co., Cleveland, Ohio	Cut back of asphalts, resins, plasticizer and fillers
Celcon	Celanese Plastics Corp., New York, N.Y.	Ethyl cellulose
Celluloid	Celanese Plastics Corp., New York, N.Y.	Cellulose nitrate
Celoron	Continental-Diamond Fibre Co., Newark, Del.	Molded, laminated or macerated plastics
Compar	Resistoflex Corp., Belleville, N.J.	Solution of compounded polyvinyl alcohol. Solution for dipping or painting
DC 2103	Dow Corning Corp., Midland, Mich.	Silicone bonding resin for plastic laminates
Dilecto	Continental-Diamond Fibre Co., Newark, Del.	Laminated sheets, rods, and tubes
Formica CN-7	Formica Insulation Co., Cincinnati, Ohio	Fabric-base phenolic laminated with chemical-resistant resin
Formica CN-22	Formica Insulation Co., Cincinnati, Ohio	Fabric-base phenolic laminated with chemical-resistant resin
Formica LN-41	Formica Insulation Co., Cincinnati, Ohio	Fine-weave fabric laminated with melamine resin

Forticel	Celanese Plastics Corp., New York, N.Y.	Cellulose propionate
Geon	B. F. Goodrich Chemical Co., Cleveland, Ohio	Polyvinyl chloride plastics
Haveg 41	Haveg Corp., Newark, Del.	Rigid thermosetting plastic
Haveg 43	Haveg Corp., Newark, Del.	Rigid thermosetting plastic
Haveg 48	Haveg Corp., Newark, Del.	Rigid thermosetting plastic
Haveg 60	Haveg Corp., Newark, Del.	Rigid thermosetting plastic
Haveg 63	Haveg Corp., Newark, Del.	Rigid thermosetting plastic
Heresite	Heresite & Chemical Co., Manitowoc, Wis.	Pure synthetic phenol-formaldehyde resin
Insurok	Richardson Co., Melrose Park, Ill.	Molded and laminated plastics. Sheet, rod, tube, fabricated parts, special moldings
Koroseal	B. F. Goodrich Co., Akron, Ohio	Plasticized polyvinyl chloride. Sheet lining, packing
Kriston	B. F. Goodrich Chemical Co., Cleveland, Ohio	Allyl ester thermosetting materials
Lamicoid	Mica Insulator Co., Schenectady, N.Y.	Phenolic laminate, fabric base. Sheets
Lucite	E. I. du Pont de Nemours & Co., Wilmington, Del.	Acrylic resin; sheets, rods, tubes, moldings
Lumarith	Celanese Plastics Corp., New York, N.Y.	Cellulose acetate
Micarta	Westinghouse Electric Corp., Pittsburgh, Pa.	Laminated plastics, fabric or kraft base. Sheets, channels, angles, molded shapes
Nixon CA (Nixonite)	Nixon Nitration Works, Nixon, N.J.	Cellulose acetate. Sheets, rods, molding powders
Nixon CN (Nixonoid)	Nixon Nitration Works, Nixon, N.J.	Cellulose nitrate. Sheets, rods, tubes
Nixon EC	Nixon Nitration Works, Nixon, N.J.	Ethyl cellulose. Molding powders
Nukemite	Nukem Products Corp., Buffalo, N.Y.	Synthetic resin sheet and coating
Nylon	E. I. du Pont de Nemours & Co., Wilmington, Del.	Polyamides; flake, sheet, extrusions, moldings; brush filament
Panelyte	St. Regis Paper Co., New York, N.Y.	Laminated resinous plastic. Sheets, rods, tubes, fabricated parts, etc.
Permanite	Maurice A. Knight, Akron, Ohio	Furane base resin. Laminates, fabricated shapes
Phenolite	National Vulcanized Fibre Co., Wilmington, Del.	Laminated phenolics. Sheet, tube, rod
Plexene	Rohm & Haas Co., Philadelphia, Pa.	Modified styrene copolymer molding powder
Plexiglas	Rohm & Haas Co., Philadelphia, Pa.	Acrylic resin. Cast sheets, rods, molding powder
Polythene	E. I. du Pont de Nemours & Co., Wilmington, Del.	Polyethylene. Sheet, rod, tube, molding powders, film, filament. Pipe, pipe lining, gaskets, etc.
Pyroflex construction	Maurice A. Knight, Akron, Ohio	Thermoplastic resin lining plus steel, brick, etc., to make a functional unit
Resilon	U.S. Stoneware Co., Akron, Ohio	Bituminous linings and membranes
Resistoflex	Resistoflex Corp., Belleville, N.J.	Compounded modified polyvinyl alcohol. Hose, sheet, molded parts
Saran	Dow Chemical Company, Midland, Mich.	Vinyl chloride-vinylidene chloride copolymer. Pipe, pipe fittings, tube, tube fittings
Sauereisen No. 44	Sauereisen Cement Co., Pittsburgh, Pa.	Bituminous-base, nonhardening plastic. Impervious linings on tanks, sewers, etc.

Materials	Manufacturer	Description
Sealon	Maurice A. Knight, Akron, Ohio	Polyvinyl chloride elastomer. Tank linings, sheets, gaskets
Synthane	Synthane Corp., Oaks, Pa.	Fabrics, paper or asbestos bonded with phenolic or melamine resin
Teflon	E. I. du Pont de Nemours & Co., Wilmington, Del.	Polymerized tetrafluoroethylene. Rods, tubes, sheets, beading, gaskets, thin tapes
Tenite I	Tennessee Eastman Corp., New York, N.Y.	Cellulose acetate thermoplastic molding material
Tenite II	Tennessee Eastman Corp., New York, N.Y.	Cellulose acetate butyrate thermoplastic molding material
Textolite cold molded	General Electric Co., Pittsfield, Mass.	Cement, bitumen or phosphoric acid base. Asbestos filled
Textolite laminated	General Electric Co., Pittsfield, Mass.	Phenolic, melamine and silicone laminates. Paper, fabric, asbestos or glass base
Textolite molded	General Electric Co., Pittsfield, Mass.	Phenolic, modified phenolic or rubber phenolic. Wood flour, cotton flock, rag or mineral filled
Tygon	U.S. Stoneware Co., Akron, Ohio	Synthetic compounds. Linings, tubing, etc.
Vimlite	Celanese Plastics Corp., New York, N.Y.	Mesh reinforced plastic
Vulcanized fibre	National Vulcanized Fibre Co., Wilmington, Del.	Sheets, tubes, rod
Westinghouse Micarta	Westinghouse Electric Corp., Pittsburgh, Pa.	Laminated sheets, rods, tubes, special shapes
Zerok	Atlas Mineral Products Co., Mertztown, Pa.	Polyvinyl chloride. Tank linings and coatings
	Rubber	
Ace hard rubber	Amer. Hard Rubber Co., Butler, N.J.	Vulcanized rubber. Rod, sheet, tube, molded parts, linings, pipe, fittings, etc.
Ace soft rubber	Amer. Hard Rubber Co., Butler, N.J.	Soft rubber. Linings, molded parts
Acidseal E	B. F. Goodrich Co., Akron, Ohio	Natural rubber sheet lining for tanks and misc. metal parts
Acidseal MA and PA	B. F. Goodrich Co., Akron, Ohio	Natural rubber sheet lining for tanks and misc. metal parts
Armstrong	Armstrong Cork Co., Lancaster, Pa.	Buna-N base gaskets
Armstrong	Armstrong Cork Co., Lancaster, Pa.	Neoprene-base gaskets
Armstrong	Armstrong Cork Co., Lancaster, Pa.	Thiokol-base gaskets
Armstrong	Armstrong Cork Co., Lancaster, Pa.	Cork-buna N base gaskets
Armstrong	Armstrong Cork Co., Lancaster, Pa.	Cork-neoprene base gaskets
Armstrong	Armstrong Cork Co., Lancaster, Pa.	Cork-Thiokol gaskets
Boston	Boston Woven Hose & Rubber Co., Boston, Mass.	Conveyor and transmission belt, hose, mechanical goods
Butyl (GR-I)	Stanco Distributors, Inc., New York, N.Y.	Solid copolymer of isobutylene and isoprene
Crane	Crane Packing Co., Chicago, Ill.	Packing and mechanical seals
Custoplast	Custodis Construction Co., New York, N.Y.	Soft rubber and neoprene tank linings

Dayton	Dayton Rubber Mfg. Co., Dayton, Ohio	Oilproof rubber belt, transmission belt
Firestone	Firestone Tire & Rubber Co., Akron, Ohio	Vibration dampeners, adhesives, sheet, tape, hose, belting, fabric, moldings, extrusions
Garlock	Garlock Packing Co., Palmyra, N.Y.	Gaskets, packings, moldings, Klozure oil seals
Gates	Gates Rubber Co., Denver, Colo.	Belts, hose, moldings
G. E. silicone rubber	General Electric Co., Pittsfield, Mass.	Sheets, extruded shapes, molded parts, coating pastes, foam, gaskets
Greene-Tweed	Greene, Tweed & Co., New York, N.Y.	Packing, gaskets, sheet
Herecrol	Heresite & Chemical Co., Manitowoc, Wis.	Butadiene acrylonitrile product. Vulcanized or uncompounded
Hewitt	Hewitt Rubber Div., Hewitt-Robins, Inc., Buffalo, N.Y.	Hose, belting
Hycar	B. F. Goodrich Chemical Co., Cleveland, Ohio	Nitrile type synthetic rubber
Jenkins	Jenkins Bros. Rubber Div., Bridgeport, Conn.	Mechanical goods, packing, valve disks, tape, moldings, extrusions
Johns-Manville	Johns-Manville Sales Corp., New York, N.Y.	Gaskets
Linear	Linear Packing & Rubber Co., Philadelphia, Pa.	Packing
Luzerne	Luzerne Rubber Co., Trenton, N.J.	Hard rubber pipe, fittings, valves, shapes, tanks, lining
Manhattan	Manhattan Rubber Mfg. Div., Passaic, N.J.	Crude and synthetic rubber linings
Neobon	Atlas Mineral Products Co., Mertztown, Pa.	Neoprene-base lining for tanks, fans, fume ducts, etc.
Neoprene	E. I. du Pont de Nemours & Co., Wilmington, Del.	Polymer of chloroprene. Crude neoprene for compounding and curing
Neoprene	Custodis Construction Co., New York, N.Y.	Synthetic rubber acidproof membrane
Paramount	Paramount Rubber Co., Detroit, Mich.	Neoprene, Buna S, natural rubber. Sheets for tank lining
Parlon	Hercules Powder Co., Wilmington, Del.	Chlorinated rubbers. Used as a base for concrete paints
Perbunan (GR-A)	Stanco Distributors, Inc., New York, N.Y.	Copolymer of butadiene and acrylonitrile. Solid sheets
Permobond natural (soft)	U.S. Rubber Co., New York, N.Y.	Linings for tanks, pipes, fittings, valves
Permobond natural (hard)	U.S. Rubber Co., New York, N.Y.	
Permobond GR-S (soft)	U.S. Rubber Co., New York, N.Y.	
Permobond GR-S (hard)	U.S. Rubber Co., New York, N.Y.	
Permobond GR-A (soft)	U.S. Rubber Co., New York, N.Y.	
Permobond GR-A (hard)	U.S. Rubber Co., New York, N.Y.	
Permobond GR-M (soft)	U.S. Rubber Co., New York, N.Y.	
Permobond GR-P (soft)	U.S. Rubber Co., New York, N.Y.	
Permobond GR-I	U.S. Rubber Co., New York, N.Y.	
Plioweld	Goodyear Tire & Rubber Co., Akron, Ohio	Rubber-lined tanks, pipe, etc.
Rewbon	Atlas Mineral Products Co., Mertztown, Pa.	Natural rubber
Saniprene	B. F. Goodrich Co., Akron, Ohio	Natural rubber sheet lining for tanks and misc. metal parts
Self-vulcanizing	Self Vulcanizing Rubber Co., Chicago, Ill.	Linings and coatings
Silastic	Dow Corning Corp., Midland, Mich.	Silicone rubber compounded with inorganic fillers
Stokes	Stokes Molded Prods., Trenton, N.J.	Hard rubber pipe, containers, fittings, misc. moldings and extrusions
Superflexite	B. F. Goodrich Co., Akron, Ohio	Flexible, natural rubber sheet lining for tanks and misc. metal parts

Materials	Manufacturer	Description
Tensilgrip	Amer. Wringer Co., Woonsocket, R.I.	Natural and synthetic rubber-lined tanks, pipe, pumps, ducts, etc.
Thermoid	Thermoid Rubber Div., Trenton, N.J.	Rubber hose; various types
Thiokol	Thiokol Corp., Trenton, N.J.	Organic polysulphide rubber. Forms: solid, water dispersion or viscous liquid
Triflex	B. F. Goodrich Co., Akron, Ohio	Hard-rubber layer sandwiched between two soft rubber layers. Sheet lining for tanks and misc. metal parts
Vistanex	Stanco Distributors, Inc., New York, N.Y.	Polymerized isobutylene. Viscous liquid to solid, depending on mol. wt.
Vulcalock	B. F. Goodrich Co., Akron, Ohio	Adhesive for rubber-to-steel bonding
Vulcanized	Vulcanized Rubber Co., New York, N.Y.	Hard and semihard moldings

INDEX

(Principal references are in **boldface** type)