Acrylic and Vinyl Fibers

1972

Marshall Sittig

Acrylic and Vinyl Fibers

1972

Marshall Sittig

Thirty-Six Dollars

NOYES DATA CORPORATION
Noyes Building
Park Ridge, New Jersey 07656, U.S.A.

Copyright © 1972 by Marshall Sittig
No part of this book may be reproduced in any form
without permission in writing from the Publisher.
Library of Congress Catalog Card Number: 72-185165
ISBN: 0-8155-0430-6
Printed in the United States

FOREWORD

The detailed, descriptive information in this book is based on U.S. patents since 1965 relating to acrylic, modacrylic, and vinyl fibers.

This book serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. patent literature in this field. By indicating all the information that is significant, and eliminating legalistic phraseology, this book presents an advanced commercially oriented review of modern acrylic and vinyl fibers technology.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure".

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development.

These publications are bound in paper in order to close the time gap between "manuscript" and "completed book". Industrial technology is progressing so rapidly that hard cover books do not always reflect the latest developments in a particular field, due to the longer time required to produce a hard cover book.

The Table of Contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor, and patent number help in providing easy access to the information presented here.

CONTENTS AND SUBJECT INDEX

INTRODUCTION 1

1. ACRYLONITRILE MONOMER MANUFACTURE 2
From Propylene, Ammonia and Oxygen 2
Chevron Research Process 2
Degussa Process 4
Farbenfabriken Bayer Process 6
Knapsack-Griesheim Process 14
Lummus Co. Process 21
Montecatini Edison Process 22
Monsanto Process 24
Osterreichische Stickstoffwerke Process 26
Snam Progetti Process 29
Standard Oil Co. (Ohio) Process 29
Ugine Kuhlmann Process 34
From Ethylene, Hydrogen Cyanide and Oxygen 40
Asahi Process 40
From Acetylene and Hydrogen Cyanide 42
American Cyanamid Process 42
Knapsack AG Process 45
Phillips Petroleum Process 48
From Acrolein Cyanohydrin 50
Knapsack-Griesheim Process 50
By Dehydrogenation of Propionitrile 51
Asahi Process 51
Eastman Kodak Process 52

2. ACRYLONITRILE POLYMER MANUFACTURE 54
Emulsion Polymerization 54
Crylor Process 54
Monsanto Process 55
Solution Polymerization 57
American Cyanamid Process 57
Eastman Kodak Process 58
Monsanto Process 60
Rhone-Poulenc Process 64
Snia Viscosa Process 68
Stoy Process 71
Toho Beslon Process 75
VEB Chemiefaserwerk Friedrich Engels Process 77
Suspension Polymerization 80
Asahi Process 80
UCB Process 84

此为试读,需要完整PDF请访问: www.ertongbook.com

3. POLYACRYLONITRILE SPINNING SOLUTION MANUFACTURE 88
American Cyanamid Process 88
B.A.S.F. Process 88
Rhone-Poulenc Process 90

4. SPINNING ACRYLONITRILE-BASED FIBERS 92
Dry Spinning 92
Du Pont Process 92
Melt Spinning 97
Sun-Chiang Process 97
Wet Spinning 99
Asahi Process 99
Courtaulds Process 99
Japan Exlan Co. Process 99
Mitsubishi Process 100
Monsanto Process 101
Toyo Rayon Process 106
Composite Fiber Manufacture 107
Japan Exlan Co. Process 107
Kanegafuchi Process 108

5. VINYL CHLORIDE MONOMER MANUFACTURE 111
By Oxychlorination of Ethylene 111
Pullman Process 111
Toyo Koatsu Process 115
By Oxychlorination of Ethane 117
Lummus Co. Process 117
Princeton Chemical Research Process 121
By Sulfochlorination of Ethane 125
Schuman Process 125
By Cracking of Ethylene Dichloride 129
Ethyl Corp. Process 129
Knapsack Process 131
Montecatini Process 133
Pechiney-Saint Gobain Process 136
From Acetylene and Hydrogen Chloride 138
Crawford & Russell Process 138
Dynamit Nobel Process 140
Japan Gas-Chemical Process 144
Knapsack Process 147
Solvay Process 151
By Reaction of Methane and Chlorine 154
Shell Process 154

6. VINYL CHLORIDE POLYMER MANUFACTURE 160
Emulsion Polymerization 160
Sumitomo Process 160
Suspension Polymerization 161
Monsanto Process 161
Pechiney-Saint Gobain Process 164
Sartomer Resins Process 167
Fluidized State Polymerization 168
Chatillon Process 168
Montecatini Edison Process 170
Phillips Petroleum Process 173
Solution Polymerization 176
Blaw-Knox Process 176
Mass Polymerization 180
Dow Process 180

Pechiney-Saint Gobain Process 182
Phillips Petroleum Process 194
Reactor Cleanup 197
Nippon Carbide Process 198

7. POLYVINYL CHLORIDE FIBER MANUFACTURE 199
Dry Spinning 199
Teijin Process 199
Melt Spinning 201
Pechiney-Saint Gobain Process 201
Wet Spinning 202
Chatillon Process 202

8. VINYL ACETATE MONOMER MANUFACTURE 206
From Acetylene and Acetic Acid 206
Blaw-Knox Process 206
Distillers Co. Ltd. Process 211
Farbwerke Hoechst Process 214
Rhone-Poulenc Process 214
From Ethylene, Acetic Acid and Oxygen 216
Celanese Process 217
Du Pont Process 227
Farbwerke Hoechst Process 230
W.R. Grace Process 232
Knapsack AG Process 237
Kurashiki Rayon Process 237
National Distillers Process 237
Union Carbide Process 239
Union Oil Co. Process 240

9. VINYL ACETATE POLYMER MANUFACTURE 255
Emulsion Polymerization 255
Consortium fur Elektrochemische Industrie Process 255
Solution Polymerization 257
Du Pont Process 257
Farbwerke Hoechst Process 258
Copolymerization with Ethylene 259
National Distillers Process 259

10. POLYVINYL ALCOHOL PRODUCTION 261
From Polyvinyl Acetate 261
Kurashiki Rayon Process 261
Masuda-Konishi Process 265
From Ethylene-Vinyl Acetate Copolymers 267
Kurashiki Rayon Process 267

11. POLYVINYL ALCOHOL FIBER PRODUCTION 269

12. ACRYLIC ESTER MONOMER MANUFACTURE 271
Production by Propylene Oxidation 271
Knapsack AG Process 271
Production by Oxidation of Acrolein 276
Distillers Co. Ltd. Process 276
Montecatini Edison Process 278
Production by Oxidation of Isobutane 281
Halcon International Process 281
Production from Methacrylaldehyde 282
Gulf Process 282
Production by Hydrolysis of Acrylonitrile 284

Standard Oil Co. (Ohio) Process 284
Production from Acetone Cyanohydrin 286
Mitsubishi Rayon Process 286
Production from Alkyl Esters and Formaldehyde 288
Eastman Kodak Process 288
Production by Cleavage of Acrylic Ester Polymers 288
Degussa Process 288
Production by Carbonylation of Methylacetylene 290
National Lead Process 290
Production by Esterification of Acrylic Acid 290
Asahi Process 290
Distillers Co. Ltd. Process 291
Mitsubishi Process 292
Montecatini Edison Process 294

13. ACRYLIC ESTER POLYMER MANUFACTURE 296
Emulsion Polymerization 296
B.A.S.F. Process 296
Colloids, Inc. Process 297
ICI Process 299

14. VINYLIDENE CHLORIDE MONOMER PRODUCTION 302
Monomer Stabilization 302
PPG Process 302

15. VINYLIDENE CHLORIDE POLYMER PRODUCTION 305
Emulsion Polymerization 305
Dynamit Nobel Process 305
Johns-Manville Process 307

16. POLYVINYLIDENE CHLORIDE FIBER MANUFACTURE 308

17. VINYL FLUORIDE MONOMER PRODUCTION 309
From Acetylene and Hydrogen Fluoride 309
Diamond Alkali Process 309
Du Pont Process 312
Dynamit Nobel Process 313
Phillips Petroleum Process 314
Ugine Kuhlmann Process 317
From Vinyl Chloride and Hydrogen Fluoride 317
Montecatini Edison Process 317

18. POLYVINYL FLUORIDE PRODUCTION 318
Suspension Polymerization 318
Daikin Kogyo Process 318
Diamond Shamrock Process 318
Du Pont Process 318

19. POLYVINYL FLUORIDE FIBER MANUFACTURE 321
Wet Spinning 321
Diamond Shamrock Process 321

20. FUTURE TRENDS 324

COMPANY INDEX 325
INVENTOR INDEX 326
U.S. PATENT NUMBER INDEX 329

INTRODUCTION

Acrylic fibers have been produced in quantity since the late 1940's. Although polyesters and polyamides continue to be the two largest volume synthetic fibers, acrylics are an important member of the top three synthetic fibers.

Acrylic fibers, normally made in staple form, are the most wool-like of the noncellulosic fibers. With their wool-like feel, their ability to retain shape and to resist deterioration from sunlight, weather, oil and chemicals, the acrylics are employed for many types of apparel.

The largest quantities of acrylic fibers are produced in the U.S., Japan, West Germany and the United Kingdom, in that order, as reviewed in "Industrial Fibres," London, Commonwealth Secretariat (1970).

The term "acrylic fiber" is applied by Federal Trade Commission definition to "a manufactured fiber in which the fiber-forming substance is any long chain synthetic polymer composed of at least 85% by weight of acrylonitrile units". Then the term "modacrylic" is applied to similar materials "composed of at least 35% but not more than 85% of acrylonitrile units".

Comonomers commonly used in the copolymers of modacrylic fibers are vinyl chloride and vinylidene chloride. The modacrylic fibers have a silk-like feel with the added advantage of being strong and hard wearing, plus the important property of being inherently flameproof. Their main uses have been in garments, curtains and filter cloths.

The manufacture and properties of acrylic and modacrylic fibers have been reviewed at some length in Chapter 12 of "Development Prospects of the Man-Made Fiber Industry," Tokyo, Japan Chemical Fibres Association (1966) and also in a supplement to European Chemical News for Oct. 29, 1971.

In addition to the fibers commonly known as acrylic fibers there are other fibers derived from vinyl monomers which are worthy of discussion here. These include polyvinyl chloride fibers, polyvinyl alcohol fibers and polyvinyl fluoride fibers.

Vinyl polymers are of course important in their own right apart from their utility in the manufacture of acrylic fibers. Thus, in this book, the manufacture of a variety of vinyl polymers (and of the monomers from which they are produced) is described.

ACRYLONITRILE MONOMER MANUFACTURE

Acrylonitrile monomer manufacture is the key process en route to acrylic polymers and thus to acrylic fibers. A review of manufacturing methods, markets, and economics for acrylonitrile monomer has been presented by R.B. Stobaugh, S.G.M. Clark and G.D. Camirand of Harvard Business School in Hydrocarbon Processing for January 1971, pp. 109-120.

FROM PROPYLENE, AMMONIA AND OXYGEN

By far the most significant process development relating to acrylonitrile in recent years and indeed one of the most important developments in industrial organic chemistry has been the ammonoxidation process for the manufacture of acrylonitrile from propylene.

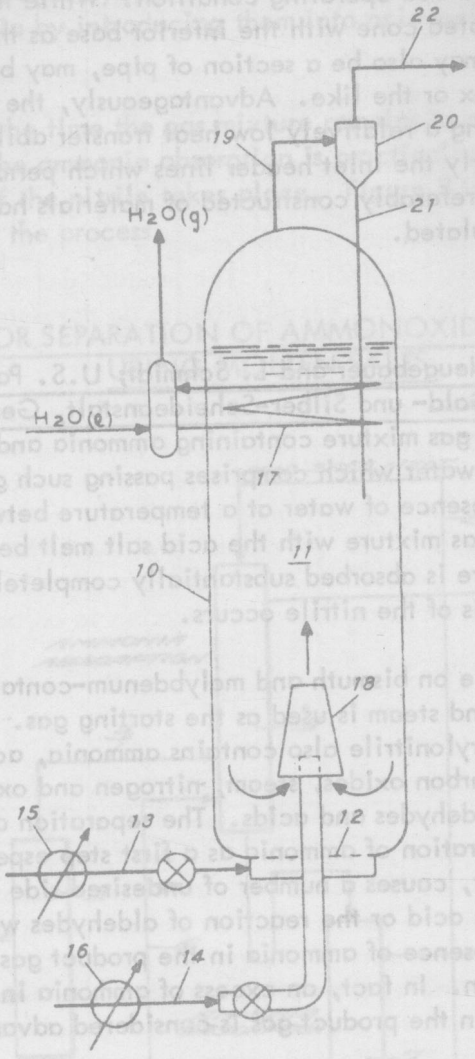
According to Chemical Week for March 1, 1972 new catalysts are now available for this process which will boost yields of acrylonitrile by 30 to 40%. It may well be an iron-modified bismuth phosphomolybdate and is being marketed by Vistron Corp., a subsidiary of Standard Oil Co. (Ohio).

Chevron Research Process

A process developed by M.F. Hughes and J.R.B. Ellis; U.S. Patent 3,501,517; March 17, 1970; assigned to Chevron Research Company is one in which the fluid bed reaction system is used both as a reaction quenching means and as a reactor. Air, ammonia and hydrocarbon feed, one or more of which is preheated, are contacted concurrently in the fluid bed and a local short duration ammonoxidation condition is generated. An indirect heat exchanger located in the dense phase of the fluid bed maintains the quenching temperature in the balance of the bed resulting in short contact times at ammonoxidation temperatures and substantial reductions in overoxidation, i.e., improved selectivities for the production of nitriles.

Figure 1 shows the essential form of apparatus which may be used for the conduct of this process. As shown in the figure, there is provided a reactor which is an essentially vertical chamber 10 capable of containing at elevated temperatures an operating ebullient fluidized-solid bed having a diameter in the range from about 2 inches up to 10 feet and larger, and having a vertical height of from about 3 to 30 feet, plus about 10% of the expanded fluid bed depth for free space above the bed, containing the bed of fluidized solids 11, as well as a base grid 12, connecting inlet gas stream headers 13 and 14, inlet line appurtenant

FIGURE 1: FLUID BED REACTOR FOR AMMONOXIDATION OF PROPYLENE



Source: M.F. Hughes and J.R.B. Ellis; U.S. Patent 3,501,517; March 17, 1970

elements, such as temperature control elements 15 and 16, a fluid bed temperature control means 17 located in the continuous fluid bed phase, a reaction zone holder 18, an exit header 19, a cyclone 20 for the disengagement of catalyst fines from the effluent gas stream, a line to return the thus recovered fines to the reaction zone proper 21, and an exit header line 22 for the delivery of the reaction product-containing gas stream to the product recovery facility.

While the heat exchange means 17 is shown as a steam generator coil located in the downstream portion of the fluid bed, other equivalent heat exchange means may be employed to maintain the general fluid bed temperature, and the exchanger(s) can be located in closer approximation to the reaction zone holder, so long as the exchanger does not seriously

此为试读,需要完整PDF请访问: www.ertongbook.com

interfere with the generation of the local oxidizing conditions and with the maintenance of the fluid bed in a normal fluid bed operating condition. While the reaction zone holder 18 is indicated as being a truncated cone with the inferior base as the exit port for the reaction product mixture, the holder may also be a section of pipe, may be in the form of a venturi nozzle, or an open-ended box or the like. Advantageously, the reaction zone holder is constructed of materials having a relatively low heat transfer ability, for example of a ceramic material, and similarly the inlet header lines which permit the introduction of superheated gas streams are preferably constructed of materials having low heat transfer ability or are adequately insulated.

Degussa Process

A process developed by W. Neugebauer and L. Schmidt; U.S. Patent 3,386,804; June 4, 1968; assigned to Deutsche Gold- und Silber-Scheideanstalt, Germany is a process for the separation of ammonia from a gas mixture containing ammonia and a gas phase organic nitrile preferably in the presence of water which comprises passing such gas mixture through an acid salt melt preferably in the presence of water at a temperature between about 90° and 300°C., the period of contact of the gas mixture with the acid salt melt being sufficiently long that the ammonia in the gas mixture is absorbed substantially completely and sufficiently short that substantially no hydrolysis of the nitrile occurs.

In the synthesis of acrylonitrile on bismuth and molybdenum-containing catalysts, a mixture of propylene, ammonia, air and steam is used as the starting gas. The product gas leaving the reaction in addition to acrylonitrile also contains ammonia, acetonitrile, hydrocyanic acid, propylene, acrolein, carbon oxides, steam, nitrogen and oxygen, as well as small amounts of various nitriles, aldehydes and acids. The separation and purification of the acrylonitrile requires the separation of ammonia as a first step especially as ammonia, because of the presence of water, causes a number of undesired side reactions such as the polymerization of hydrocyanic acid or the reaction of aldehydes with hydrocyanic acid to produce cyanhydrins. The presence of ammonia in the product gas cannot be avoided because of incomplete conversion. In fact, an excess of ammonia in the starting gas and a minimum content of ammonia in the product gas is considered advantageous for a high yield of acrylonitrile.

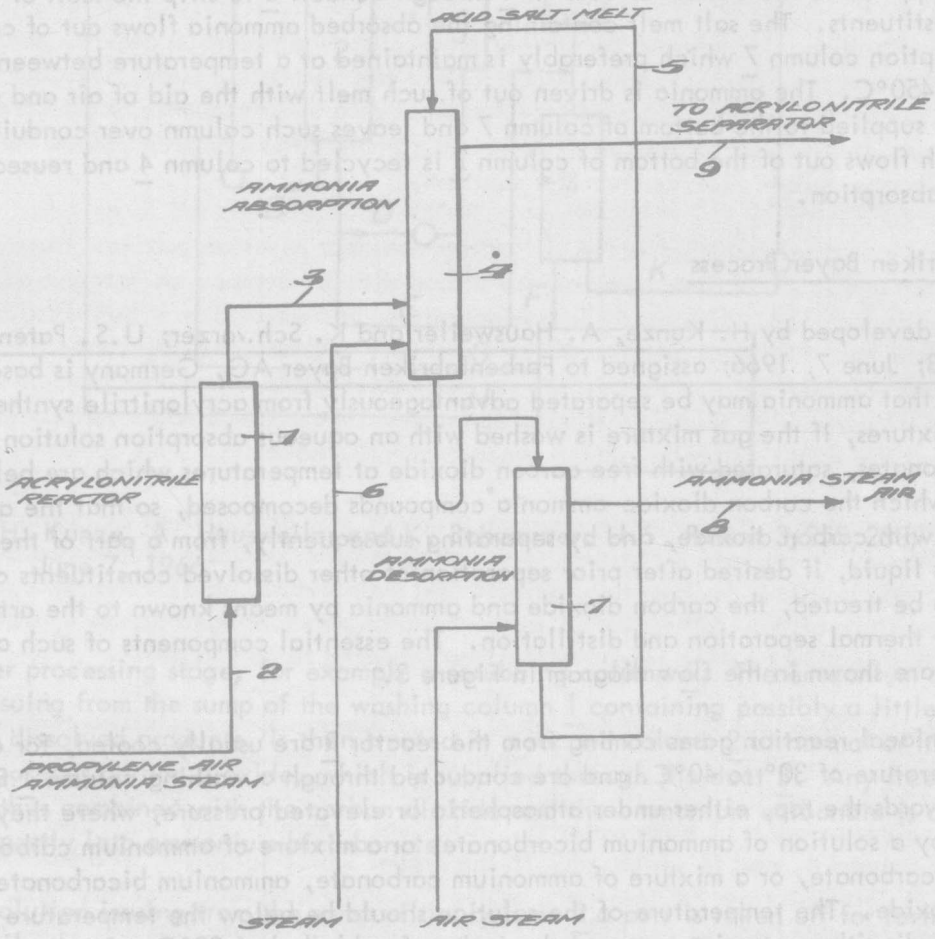
A process is known in which the product gas is washed with dilute sulfuric acid after it leaves the reactor. According to this procedure all of the ammonia is removed from the product gas stream to produce a dilute solution of ammonium bisulfate. This solution can be neutralized with ammonia and evaporated to dryness to produce ammonium sulfate. This procedure leaves much to be desired if one wishes to recover the ammonia in free form. Furthermore, in addition to ammonia, portions of nitriles, hydrocyanic acid and acrolein are taken up in the sulfuric acid used and these must be removed by distillation.

In the development of this process, it was found that ammonia can be separated and also recovered from gas phase nitriles or such gas phase nitriles containing water vapor or other gas phase mixtures containing nitriles and water vapor if they are passed through an acid melt at a temperature between 90° and 300°C., preferably between 125° and 250°C., and maintained in contact therewith only for such a short time that hydrolysis of the nitrile does not occur and then, if desired, heating the melt further to a temperature between 300° and

500°C., preferably between about 350° and 450°C., to effect desorption of the ammonia taken up by the melt. It was unexpected that such a separation would be successful as it is known that nitriles can be hydrolyzed to their corresponding acids with recovery of their nitrile nitrogen as ammonia by introducing them into acid melts in the presence of water at temperatures up to 250°C.

In this process however, the time the gas mixture remains in contact with the acid salt melt is sufficiently long that the ammonia absorption is practically quantitative but sufficiently short that no hydrolysis of the nitrile takes place. Figure 2 is a flow diagram which further illustrates the conduct of the process.

FIGURE 2: PROCESS FOR SEPARATION OF AMMONOXIDATION REACTION PRODUCTS USING MOLTEN SALTS



Source: W. Neugebauer and L. Schmidt; U.S. Patent 3,386,804; June 4, 1968

Referring to such flowsheet, a gas mixture of propylene, air, ammonia and steam is supplied through conduit 2 to reactor 1 filled with a bismuth and molybdenum containing catalyst. The propylene is converted to the desired product by ammonoxidation. In addition, the by-products acetonitrile and hydrocyanic acid are also produced. Furthermore, the product gas leaving reactor 1 also contains carbon oxides, small quantities of acrolein, acids and higher nitriles as well as unconverted ammonia, unconverted propylene, steam, nitrogen and oxygen. The product gas is supplied over conduit 3 to ammonia absorption column 4 which is also supplied over conduit 5 with a melt of sodium bisulfate and potassium bisulfate in a molar ratio of 1.15:1. The entire quantity of ammonia and a part of the steam contained in the product gases are absorbed in absorption column 4 which is preferably maintained at a temperature between about 125° and 250°C. The product gas which has been freed of ammonia leaving column 4 through line 9 is supplied to an acrylonitrile separation operation which is carried out by methods known per se.

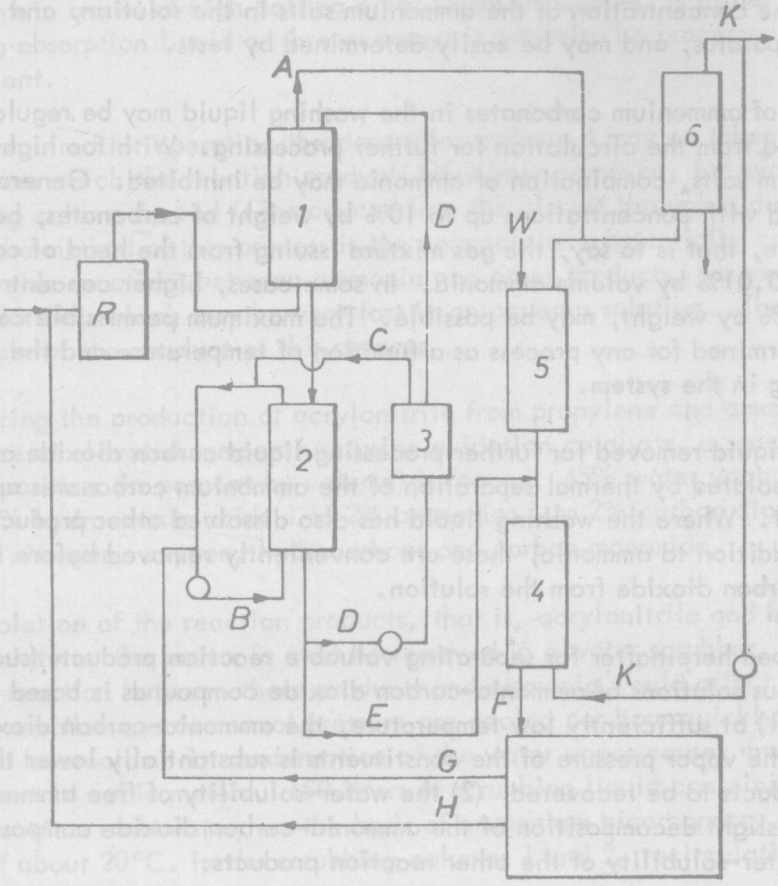
In order to remove small quantities of dissolved or entrained quantities of organic substances, steam is supplied to the bottom of column 4 through conduit 6 to strip the melt of such organic constituents. The salt melt containing the absorbed ammonia flows out of column 4 into desorption column 7 which preferably is maintained at a temperature between about 350° and 450°C. The ammonia is driven out of such melt with the aid of air and steam which are supplied to the bottom of column 7 and leaves such column over conduit 8. The melt which flows out of the bottom of column 7 is recycled to column 4 and reused for the ammonia absorption.

Farbenfabriken Bayer Process

A process developed by H. Kunze, A. Hausweiler and K. Schwarzer; U.S. Patent 3,255,233; June 7, 1966; assigned to Farbenfabriken Bayer AG, Germany is based on the discovery that ammonia may be separated advantageously from acrylonitrile synthesis product gas mixtures, if the gas mixture is washed with an aqueous absorption solution of ammonium carbonates, saturated with free carbon dioxide at temperatures which are below the range at which the carbon dioxide-ammonia compounds decomposed, so that the ammonia is combined with carbon dioxide, and by separating subsequently, from a part of the circulating absorption liquid, if desired after prior separation of other dissolved constituents of the gas mixture to be treated, the carbon dioxide and ammonia by means known to the art, for example, by thermal separation and distillation. The essential components of such a process operation are shown in the flow diagram in Figure 3.

The ammoniacal reaction gases coming from the reactor R are usually cooled, for example to a temperature of 30° to 40°C. and are conducted through a washing column 1 from the bottom towards the top, either under atmospheric or elevated pressure, where they are scrubbed by a solution of ammonium bicarbonate, or a mixture of ammonium carbonate, ammonium bicarbonate, or a mixture of ammonium carbonate, ammonium bicarbonate and carbon dioxide. The temperature of the solution should be below the temperature range of the carbon dioxide-ammonium compounds, and preferably below 30°C., for example between 15° and 25°C. During this process, the ammonia is removed from the countercurrent of the reaction gas and converted into ammonium carbonate. Finally, also a small proportion of the other products contained in the gas is dissolved, provided that these are soluble in water. The ammonia-free gas issues from the column 1 and may be conducted by a duct A

FIGURE 3: PROCESS FOR AMMONIA SEPARATION FROM AMMONOXIDATION REACTION PRODUCTS USING AQUEOUS AMMONIUM CARBONATE



Source: H. Kunze, A. Hausweiler and K. Schwarzer; U.S. Patent 3,255,233; June 7, 1966

to a further processing stage, for example a scrubbing column 6. The ammonium carbonate solution issuing from the sump of the washing column 1 containing possibly a little free ammonia and dissolved products, is then treated in a second column 2 at normal or higher pressure with gaseous carbon dioxide, which is supplied through the duct B. Any free ammonia present is thus combined with the carbon dioxide and the ammonium carbonate is converted wholly or partly into ammonium bicarbonate.

From the solution issuing from the sump of the column 2 a part is taken off for further processing, while the remainder is again conducted through a duct D to the washing column 1, if desired through a degassing apparatus 3, where excess carbon dioxide is removed, which is carried away through a duct C. If the reduction in the volume, caused by taking off a part of the circulating liquid is not equalized by returning it after the elimination of ammonia or within the column 1 by the water content of the gas to be treated, fresh water is

added in suitable amounts at the head of the column 1. The ratio between washing liquid and gas volume, and with this the quantity of circulating washing liquid, necessary for the complete removal of the ammonia, depends substantially on the ammonia content of the reaction gases, on the concentration of the ammonium salts in the solution, and on the construction of the apparatus, and may be easily determined by tests.

The concentration of ammonium carbonates in the washing liquid may be regulated through the amount removed from the circulation for further processing. With too high a concentration of ammonium salts, combination of ammonia may be inhibited. Generally, good results are obtained with concentrations up to 10% by weight of carbonates, based on ammonium bicarbonate, that is to say, the gas mixture issuing from the head of column 1 contains less than 0.01% by volume ammonia. In some cases, higher concentration, for example, up to 20% by weight, may be possible. The maximum permissible concentration may be easily determined for any process as a function of temperature and the quantity of solution circulating in the system.

From the washing liquid removed for further processing liquid carbon dioxide and ammonia are expelled and isolated by thermal separation of the ammonium carbonates and distillation, as known to the art. Where the washing liquid has also dissolved other products from the reaction gas, in addition to ammonia, these are conveniently removed before the recovery of ammonia and carbon dioxide from the solution.

The method described hereinafter for separating valuable reaction products (such as acrylonitrile) from aqueous solutions of ammonia-carbon dioxide compounds is based on the following assumptions: (1) at sufficiently low temperature, the ammonia-carbon dioxide compounds are so stable that the vapor pressure of the constituents is substantially lower than that of the other reaction products to be recovered; (2) the water-solubility of free ammonia which may be formed by very slight decomposition of the ammonia-carbon dioxide compound, is much higher than the water-solubility of the other reaction products.

It has been found that the valuable reaction products may be expelled by means of the following method. The aqueous solution, containing ammonia-carbon dioxide compounds and other reaction products (such as acrylonitrile and hydrocyanic acid) flows through a duct E at a temperature of, say 30° to 40°C. to the head of an exchange column 4, through which flows an inert gas in countercurrent to the liquid heated to 30° to 40°C.

The gas desorbs from the solution the valuable reaction products contained therein, and corresponding to the lower partial ammonium pressure of the solution, a comparatively small amount of free ammonia. The gas then flows into the column 5, arranged above column 4 which receives amounts of fresh water W, which are comparatively small compared with the supply of column 4, and in which, due to the higher water-solubility of ammonia, mainly ammonia is absorbed from the inert gas, while the other products, together with the inert gas, leave the upper end of the column 5 in a substantially ammonia-free condition, and are conducted to a further processing stage, if desired together with the gas mixture leaving the column 1.

The sump discharge from column 5 is mixed with the charge of column 4 from the sump of which there is discharged an aqueous solution of ammonia-carbon dioxide compounds through

a duct F, from which ammonia and carbon dioxide are recovered as gases by known methods. The carbon dioxide which is recovered may be supplied through a duct G to column 2 and the gaseous ammonia through a duct H to a further processing stage. The remaining water, which may contain traces of high boiling point waste impurities, is either reintroduced into the circulating absorption liquid or thrown away; it may also be processed in a waste water purification plant.

The inert gas required for operating the desorption column 4 may be taken from the waste gas current, from which the reaction products have been removed, for example downstream of the scrubbing column 6, and is introduced into the circuit through a duct K. A particular advantage of the method of this process is the complete or substantially complete inhibition of undesirable side reactions between ammonia and other products, for example, hydrocyanic acid or acrylonitrile, which may be very fast in an aqueous solution. The following is a specific example of the conduct of this process.

Example: During the production of acrylonitrile from propylene and ammonia by reaction in the gas phase at elevated temperature using oxidation catalysts, a reaction gas with the following composition (in percent by volume) is formed: 45% water vapor; 2 to 3% acrylonitrile; 1 to 2% hydrocyanic acid; 1 to 2% ammonia; 1 to 2% carbon dioxide. The remainder consists of nitrogen, oxygen, hydrocarbons and carbon monoxide.

Prior to the isolation of the reaction products, that is, acrylonitrile and hydrocyanic acid, from this gas mixture, the ammonia must be removed in a water scrubber, because otherwise the secondary reaction between these products and ammonia would affect the yield. About 25 scm of this reaction gas at normal pressure are cooled per hour quickly to 30° to 40°C. and introduced into column 1; condensation of the water vapor causes the volume to be reduced to about 14 cubic meters. 150 liters of scrubbing liquid containing about 7 to 9% by weight ammonium carbonates, on the basis of ammonium bicarbonate, circulate at a temperature of about 20°C. in the scrubbing columns 1 and 2, recirculating about 2 to 5 times per hour.

The ammonia is removed practically completely in column 1 and in addition not more than 20% of the water-soluble organic products (hydrocyanic acid and acrylonitrile) are retained in the scrubbing liquid. From the sump of column 1, the scrubbing liquid is pumped to the head of column 2, which is under a CO_2 pressure of from 0.02 to 0.1 excess atmospheres. From the sump of column 2, the carbon dioxide regenerated scrubbing liquid is reintroduced through a cooler and an expansion vessel 3, where the excess of dissolved carbon dioxide is removed, into the head of column 1. A partial branch flow of 8 to 9 kg./hr. (that is to say, the quantity resulting from condensation of the reaction gas) is taken off and supplied to column 4.

In column 4, the acrylonitrile and hydrocyanic acid components are desorbed from the solution by a flow of inert gas at about 8 $m.^3$/hr. at 30° to 40°C., so that the sump discharge of this column is an aqueous solution of ammonium carbonates (7 to 9%) which is free of hydrocyanic acid and acrylonitrile, which is then further processed by methods known to the art. The flow of inert gas is freed from traces of ammonia in column 5, scrubbed with about 2 kg./hr. fresh water (W) at 30°C., and combined finally with the ammonia free flow of gas issuing from column 1. The combined gases pass into column 6 where they are scrubbed

此为试读,需要完整PDF请访问: www.ertongbook.com