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Isocyanates Manufacture

1972

Dr. M.W. Ranney

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FOREWORD

Dr. M.W. Ranney

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FOREWORD

The detailed, descriptive information in this book is based on U.S. patents since 1967 relating to the preparation and commercial manufacture of various isocyanates.

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 current manufacturing practices for obtaining isocyanates.

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 useful 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 contained in this volume.

CONTENTS AND SUBJECT INDEX

| | |
|---|----|
| INTRODUCTION | 1 |
| TOLUENE DIISOCYANATES | 2 |
| Phosgenation Processes | 2 |
| Apparatus for Conducting Rapid Phosgenations | 2 |
| Tubular Reactor | 8 |
| Elongated Reaction Column | 11 |
| Two-Stage High Pressure Process | 12 |
| Continuous Two-Stage Process | 17 |
| Hydrochlorination of Diamine | 21 |
| Hot Phosgenation Process | 23 |
| Nonvicinal Toluene Diisocyanates | 24 |
| Distillation and Recovery Techniques | 27 |
| Rotating Mill-Type Evaporator | 27 |
| Distillation Processes | 29 |
| Separation of Ortho Isomers | 31 |
| Distillation in Presence of Polyhydroxy Compounds | 33 |
| Crystallization and Distillation Techniques | 36 |
| Heating in Presence of Organotin Compounds | 36 |
| Phosgenation of Distillation Residue | 38 |
| Recovery of Toluenediamines | 39 |
| Stabilization and Chloride Removal Processes | 40 |
| Dilauryl Thiodipropionate | 40 |
| Aromatic Amines | 41 |
| Stabilization at Elevated Temperatures | 43 |
| Metallic Naphthenates for Chloride Removal | 44 |
| Copper Powder for Chloride Removal | 45 |
| Other Processes and Mixtures | 45 |
| Oxide of Nitrogen-Urea Reactions | 45 |
| Xylylene Dichloride and Alkali Metal Cyanate | 46 |
| Polyisocyanate Blends | 48 |
| AROMATIC ISOCYANATES | 50 |
| Polyisocyanates | 50 |
| Liquid Polyisocyanates by Stepwise Preparation | 50 |
| Liquid Methylenebis(Phenyl Isocyanate) Compositions | 52 |
| Purification of Methylenebis(4-Phenyl Isocyanate) | 53 |
| Methylene Polyisocyanate Mixtures | 55 |
| Storage Stable 4,4'-Diisocyanatodiphenylmethane | 58 |
| Polyisocyanate Mixtures | 59 |
| Polyisocyanate-Water Reaction Products | 62 |
| Fractionation of Crude Polyisocyanates | 62 |
| 3-Alkoxy-4,4'-Diisocyanatodiphenylmethanes | 69 |
| Amine Intermediates | 71 |

Contents and Subject Index

| | |
|--|-----|
| Thin Film Evaporator for Recovery | 71 |
| Organosilicones as Crystallization Stabilizers | 74 |
| Diphenyldecyl Phosphite Decolorization | 75 |
| Conversion of Nitro Compounds Using CO | 76 |
| Metal Halides-Lewis Base Complexes | 76 |
| Palladous Halide and Nitrilic Solvent | 77 |
| Cobalt Iodide Catalyst | 79 |
| Noble Metal Catalyst | 79 |
| Conversion of Azides | 82 |
| Conversion of Azo or Azoxy Compounds | 83 |
| Conversion of Nitroso Compounds | 84 |
| Primary Amine-Carbon Monoxide-Platinum Catalyst | 86 |
| Sulfonyl Isocyanates | 89 |
| Isocyanatophenylsulfonyl Isocyanates | 89 |
| Isocyanato-Substituted Sulfonyl Isocyanates | 91 |
| Organic Sulfonyl Isocyanates as Stabilizers | 93 |
| Phenylisocyanatosulfonyl Chloride | 94 |
| Other Processes | 97 |
| Hindered Isocyanates Containing Hydroxyl Groups | 97 |
| Isocyanatophenols | 98 |
| 1,4-Bis(Isocyanato)-1-Phenyltetrahydronaphthalene | 100 |
| Oxydi(p-Phenylene Isocyanate) | 103 |
| Conversion of Isonitriles | 104 |
| Decomposition of N-Haloamides | 105 |
| Decomposition of Cyclic Nitrile Sulfites | 107 |
| Terphenyl Triisocyanates | 109 |
| 4-Substituted-2,6-Toluene Diisocyanate | 111 |
| Isocyanatostilbenes | 116 |
| Tetramethyl-p-Xylylenediamine | 118 |
| 3. NONAROMATIC ISOCYANATES | 123 |
| Cycloaliphatic Polyisocyanates | 123 |
| 3-(Isocyanatomethyl)-3,5,5-Trialkylcyclohexyl Isocyanates | 123 |
| 2,4-Bis(Isocyanatocyclohexylmethyl)Cyclohexyl Isocyanate | 124 |
| 1,3,5-Cyclohexane Triisocyanate | 125 |
| Cycloaliphatic Tetraisocyanates | 127 |
| 4,4'-Methylenebis(Cyclohexyl Isocyanate) Process | 128 |
| Norbornane Diisocyanate and Tricyclic Isocyanates | 130 |
| Alkyl-Substituted Cyclohexylenediamines | 133 |
| Cycloaliphatic Di(Aminoalkanes) | 135 |
| Unsaturated Diisocyanates | 138 |
| Bis(2-Isocyanatoethyl) Fumarate | 138 |
| Water-Soluble Derivatives of Bis(2-Isocyanatoethyl) Fumarate | 143 |
| Pyrolysis of Vinyl-Substituted Isocyanurates | 144 |
| Alkenyl Isocyanates | 146 |
| Thermal Dehydrohalogenation Process | 146 |
| Other Polyisocyanates | 148 |
| Amine-Sulfonyl Isocyanate Reaction Products | 148 |
| Decomposition of Cyclic Nitrile Sulfites | 150 |
| Nitrazo Diisocyanates | 151 |
| Polyoxyalkylene Diisocyanates | 153 |
| Urethane Drying Oils | 154 |
| 1,2-Di[4-(2-Isocyanatoethyl) Phenyl]-3-Isocyanatopropane | 158 |
| Monoisocyanates | 160 |
| Carbamic Acid Ester-Isocyanate Reaction | 160 |
| Organic Chloride and Metal Cyanate Reactions | 161 |
| Thermal Cleavage of Thiocarbamic Acid Esters | 161 |
| Ether-Containing Isocyanates | 165 |
| Dicyclopentadiene Isocyanate-Vinyl Copolymers | 167 |

Contents and Subject Index

| | |
|---|-----|
| Monoisocyanates from Isocyanate Distillation Residues | 168 |
| Miscellaneous | 169 |
| Polymeric Fatty Acids as Intermediates | 169 |
| Chloride Removal | 172 |
| Dialkyl Acid Pyrophosphate Stabilizers | 173 |
| 4. HALOGEN-CONTAINING ISOCYANATES | 175 |
| Aromatic | 175 |
| Halogenation of Toluene Diisocyanate | 175 |
| Anhydrous Hydrogen Chloride-Chlorine Addition | 178 |
| Chlorination of Polyisocyanate Compositions | 180 |
| Halogenation of Alkyl-Aryl Isocyanates | 181 |
| Perchlorinated Aromatic Polyisocyanates | 184 |
| Halogenated Aromatic Isocyanates | 185 |
| Polyhalogenated Phenylene Polyisocyanates | 186 |
| Hexahalobicyclo-Diisocyanatophenyl Ethers | 187 |
| p-Chlorophenyl Isocyanate | 189 |
| 2-Chlorocarbonylphenyl Isocyanates | 189 |
| Difluoroalkylarylmethyl Isocyanates | 190 |
| Perfluorinated Aromatic Diamines | 193 |
| Aliphatic | 196 |
| 2,3-Bis(Difluoroamino)Butane-1,4-Diisocyanate | 196 |
| Trifluoroguanyl Isocyanate Derivatives | 197 |
| Trifluoromethyl Isocyanate | 200 |
| α -Halogeno Isocyanates | 201 |
| β -Chloroisocyanato Adducts of Unsaturated Oils | 202 |
| Trichlorobromoalkyl Isocyanates | 205 |
| 5. POLYUREAS, BIURETS AND SILICON-CONTAINING COMPOUNDS | 207 |
| Polyureas and Biurets | 207 |
| Polyhydroxy Diureas | 207 |
| Acylated Urea Polyisocyanates | 209 |
| Undistilled Polyisocyanate-Polyurea Coatings | 210 |
| Emulsions | 214 |
| Biuret Polyisocyanates | 217 |
| Polyether Polyisocyanato Biurets | 220 |
| Silicon-Containing Compounds | 223 |
| Isocyanato Functional Polysiloxanes as Foam Stabilizers | 223 |
| Silicon-Containing Heterocyclic Triisocyanates | 227 |
| 6. GENERAL PROCESSES | 230 |
| General Synthesis | 230 |
| Isocyanic Acid-Olefin Reactions | 230 |
| Decomposition of Cyclic Nitrile Carbonates | 232 |
| Conversion of Isocyanates to Isothiocyanates | 234 |
| Phosgenation in Presence of Weak Lewis Base | 236 |
| Temperature Controlled High Dilution Phosgenation Process | 236 |
| Phosgenation Using Amide Catalysts | 238 |
| Trialkyl Boranes as Color Stabilizers | 240 |
| 2,2-Dimethoxy Propane as Viscosity Stabilizer | 241 |
| Secondary Carbamoyl Chlorides as Intermediates | 242 |
| Diphenyl Carbonate-Amine Reaction Products | 245 |
| Miscellaneous Processes | 247 |
| Diisocyanate Dimers in Aqueous Medium | 247 |
| Isocyanate-Containing Polyisocyanate Salts | 249 |
| Ethyl-p-Hydroxybenzoate as Blocking Agent | 251 |
| COMPANY INDEX | 253 |
| INVENTOR INDEX | 254 |
| U.S. PATENT NUMBER INDEX | 256 |

INTRODUCTION

While the first organic isocyanate was prepared by Wurtz in 1849, and some industrial development began in Germany in the late 1930's, no significant commercial interest emerged until after World War II. In the 1950's, the combined research efforts of Germany and the United States, particularly in the development of viable production processes for flexible polymeric foams, fibers, coatings and elastomers created a strong demand for toluene diisocyanate.

In rigid foam applications, polyisocyanates, obtained by phosgenation of polyamines made from aniline and formaldehyde are widely used. The need for flame retardent foam products is becoming increasingly critical. Polyurethane elastomers, such as Estane (B.F. Goodrich) and Texin (Mobay) are available for processing by extrusion or injection molding. Polyurethane coatings are well-known for their chemical and abrasion resistance.

The nonpolymer uses for isocyanates include insecticides, herbicides, explosives and many biologically active products. Through the sixties, isocyanate production had an average growth rate of 24% per year and this is projected to continue, although at the slightly reduced rate of 17% per year, reaching one billion pounds in 1975. The nine major domestic producers have an estimated capacity of 400 million pounds per year of toluene diisocyanate and some 300 million pounds per year of polymeric isocyanates.

The major outlet continues to be polyurethane foams, with 48% going into flexibles and 24% into rigid foams. Approximately 21% of the domestic production is currently exported, although this will likely be difficult to sustain through the 1970's as new capacity comes on-stream overseas. Indeed, Europe, through the efforts of Gayer, Montedison, Shell, BASF, DeKachimie and Tolochimie and others may well become a net exporter of isocyanates in the next few years.

West European capacity for toluene diisocyanate, estimated at 280 MM pounds in 1970, will jump to 500 MM pounds in 1973 based on planned expansions. Capacity for methane diisocyanate will triple by 1973 reaching 200 MM pounds per year. This book describes some 170 recent processes related to improved methods of manufacture for toluene diisocyanate, polymeric isocyanates, aliphatic isocyanates and some flame retardant, halogen-containing isocyanates.

Note: Throughout this book the terms toluene diisocyanate and tolylene diisocyanate are used interchangeably.

TOLUENE DIISOCYANATES

PHOSGENATION PROCESSES

Apparatus for Conducting Rapid Phosgenations

R.M. Ewald; U.S. Patent 3,321,283; May 23, 1967; assigned to Mobay Chemical Co. describes a method and apparatus for the preparation of organic isocyanates by the phosgenation of the corresponding amine.

The process involves rapidly combining two different solutions by continuously introducing an excess of a solution of phosgene in an inert solvent into a plurality of restricted discrete dispersal zones, introducing a solution of an organic amine in an inert solvent into the dispersal zones through a plurality of passageways, continuously discharging the mixture formed in each of the dispersal zones into each of a plurality of reaction zones, such that the residence time within each of the dispersal zones is less than the half life of the phosgeneamine reaction, there being one reaction zone for each dispersal zone, subjecting each of the dispersal and reaction zones to a shearing action and collecting the product from each of the reaction zones.

The apparatus for conducting this process, includes a chamber having walls defined by a surface of rotation, and a rotor disposed and closely fitting within the chamber. The rotor has a plurality of lands and grooves, the grooves of which constitute the reaction zones. Means are provided for the introduction of phosgene solution and for the introduction of amine solution into the grooves.

Where the half life of a reaction is on the order of 0.005 to 0.1 second, it is extremely important to reduce the dispersal time especially where competing reactions lower the yield. By operating the apparatus in accordance with this process according to the method described nearly complete dispersal of one reactant in the other takes place in less time than the half life of the reaction. Thus, the reactants are completely mixed before half of the heat of reaction is evolved.

Since the reaction rate is reduced two or three fold for each 10°C. reduction in temperature, the reaction rate is reduced during the initial mixing period and the first part of the reaction period. This reduces side reactions. In addition, where solids result as in the case where amines are reacted with phosgene, formation of a heavy slurry is avoided in the initial dispersal zone.

The reaction of phosgene with amine is accomplished with the formation of HCl and phosgene vapor. These vapors cause cavitation of conventional mixing devices. By the method of this process, cavitation is avoided because it is possible to utilize lower temperatures and also because only partial reaction takes place in the initial mixing zone. The apparatus has a capacity of from about 50 to 75 million pounds per year with yields of about 94% of theoretical. The apparatus used in the process is shown in Figures 1.1a through 1.1e. Figure 1.1a is a partially cut away sectional elevation and Figure 1.1b is a cross-sectional view taken along lines 11-11 of Figure 1.1a. In these figures, a cylindrical first chamber 1 is shown having a rotor 3 coaxially disposed therein. The rotor 3 is journaled in a bearing 7 at the lower end of chamber 1.

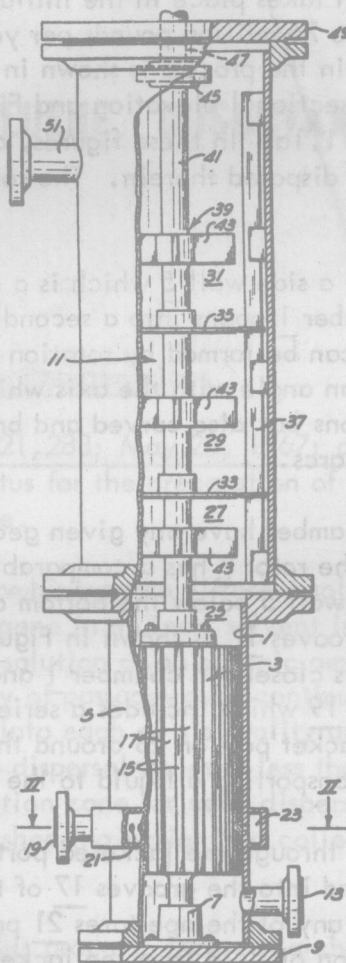
The chamber 1 itself is formed by a side wall 5 which is a surface rotation and by the bottom end wall 9. The top of the chamber 1 opens into a second chamber 11. By surface of rotation is meant any surface which can be formed by rotation of a line about an axis. This includes not only straight lines at an angle with the axis which would result in conical sections or frustoconical cross-sections but also curved and broken lines such as a series of lines which would appear as steps and arcs.

Thus, it is not essential that a chamber have any given geometrical configuration, but can be almost any design as long as the rotor 3 has a comparable design. The chamber 1 is provided with a first inlet 13 in the wall 5 below the bottom of the rotor 3. The rotor 3 itself has a plurality of lands 15 and grooves 17 as shown in Figure 1.1b which in Figure 1.1a runs the entire length. The rotor 3 fits closely in chamber 1 and rotates freely. The chamber 1 is provided with a second inlet 19 which includes a series of apertures 21 through the wall 5 of the chamber 1 and a small jacket portion 23 around the outer periphery of the chamber 1 which provides a conduit for transporting a liquid to the apertures 21.

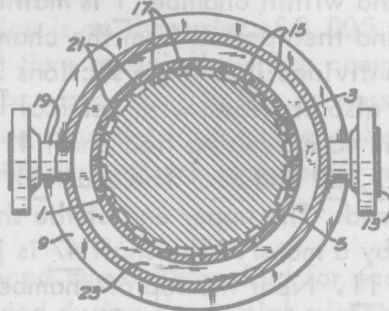
The fluid to be introduced passes through the jacketed portion 23 through the apertures 21 in the wall 5 of the chamber 1 and into the grooves 17 of the rotor 3. The lands 15 of the rotor 3, as they pass adjacent to any of the apertures 21 provided in the chamber 1 substantially prevent the introduction of fluid from the jacketed portion 23 into the chamber 1. However, when a groove 17 is adjacent an aperture 21 in the chamber wall 5, the fluid within the jacketed portion 23 is permitted to enter the chamber 1. Thus, intermittent introduction of the fluid maintained in the jacketed portion 23 into the grooves 17 is achieved.

An area 25 above the rotor 3 and within chamber 1 is maintained where the reaction mixtures or the products are collected and then passed from the chamber 1 in a body into a second chamber 11 which as shown, is divided into three sections 27, 29 and 31 by baffles 33 and 35. The second chamber 11 is also provided with vertical baffles 37 and an agitator 39 including a shaft 41 and impellers 43 extending from shaft 41. At least one impeller 43 is located in each of the sections 27, 29 and 31. The shaft 41 is coaxial with rotor 3 and mechanically connected at the lower end. The upper end of the shaft 41 is connected by a coupling 45 to a shaft 47 that is driven by a motor. The shaft 47 is journaled in a bearing in the top wall 49 of the second chamber 11. Near the top of chamber 11, there is provided a discharge outlet 51 where the reaction product is removed. This may be connected to any suitable hot phosgenation apparatus. In operation for the production of an isocyanate, a phosgene solution enters the chamber 1 through the first inlet 13 and passes in an upward direction through the grooves 17 in the rotor 3.

FIGURE 1.1: APPARATUS FOR PHOSGENATION REACTIONS

a.

(a) Sectional View

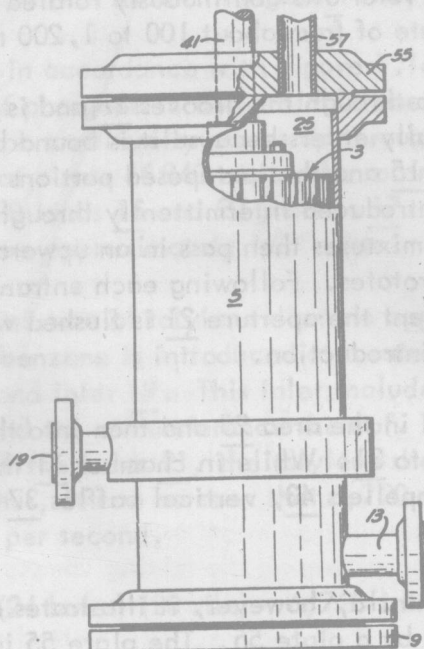
b.

(b) View Along Line II-II of Figure 1.1a

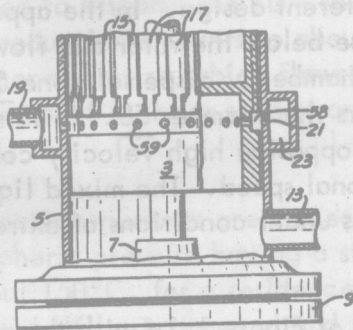
(continued)

FIGURE 1.1: (continued)

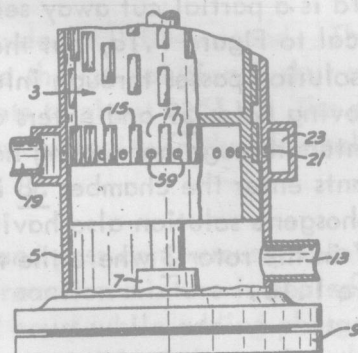
c.



d.



e.



(c)-(e) Modified Reactors

Source: R.M. Ewald; U.S. Patent 3,321,283; May 23, 1967

Toluene Diisocyanates

The portion of the grooves 17 adjacent the apertures 21 are the zones wherein the amine solution is dispersed into the phosgene solution. The area of the grooves 17 above this portion is the reaction zone. The rotor 3 is continuously rotated by means of a suitable drive mechanism (not shown), at a rate of from about 100 to 1,200 rpm.

The phosgene solution passes up through the grooves 17 and is substantially maintained within the groove 17 in which it initially enters because it is bound by the bottom of the groove 17, the sides of the adjacent lands 15 and the juxtaposed portions of the side walls 5 of the chamber 1. The amine solution is introduced intermittently through the holes 21 provided in the chamber wall 5. The reaction mixtures then pass in an upward direction in the grooves 17 while the rotor 3 continuously rotates. Following each entrance of the amine solution, the portion of the grooves 17 adjacent the aperture 21 is flushed with phosgene solution because of the continuous nature of its introduction.

The mixtures are then collected in the area 25 and then into the second chamber 11 where they pass from section 27 to 29 to 31. While in chamber 11 the mixtures are continuously agitated due to the action of impellers 43, vertical baffles 37 and horizontal baffles 33 and 35.

Figure 1.1c is similar to Figure 1.1a, however, it illustrates a modification where the chamber 1 is closed at the upper end by a plate 55. The plate 55 includes an opening in which shaft 41 is journaled and a discharge outlet 57. The phosgene and amine solutions enter through inlets 13 and 19 respectively, pass up through the grooves 17 of the rotor 3 as shown in Figure 1.1a, are collected in area 25 and then pass out through discharge outlet 57 to other apparatus which completes the reaction.

Figure 1.1d is a partial cut away section elevation of a form in which the nonmoving parts are identical to Figure 1.1a, but the rotor 3 is a different design. In the apparatus, the phosgene solution passes through inlet 13 into a space below the rotor and flows radially through moving holes 59 and enters a small mixing chamber or dispersal zone 58. The amine solution enters through nonmoving holes 21 and enters the chamber 58. In this manner, the two reactants enter the chamber 58 in a plurality of opposing high velocity continuous streams with the phosgene solution also having a high rotational speed. The mixed liquids enter the grooves 17 in the rotor 3 where the reaction proceeds under conditions of extreme turbulence as in Figure 1.1a.

The apparatus shown in Figure 1.1e is similar to that of Figure 1.1c with the exception that the rotor 3 is further modified and includes lands 15 and grooves 17 arranged in parallel fashion only in the vicinity in which the amine solution is introduced into the phosgene solution. These lands 15 and grooves 17 run only a short longitudinal length of the rotor 3. The phosgene solution enters the grooves 17 in a manner similar to that shown in Figure 1.1d by passing through holes 59 provided in the rotor 3.

The lands operate in a manner described above with regard to Figure 1.1a causing the intermittent introduction of the amine solution into the grooves 17. This modification differs from those shown in the first three figures in that the entire body of the reaction mixture is reunited shortly after the amine solution is introduced and dispersed. This portion of the rotor carries a plurality of protrusions which further agitate and shear the reaction mixture.

Because of the pressure behind the introduction of both of the solutions, the reaction mixture continuously passes in an upward direction until it either passes out of a discharge outlet or into a second reaction chamber as that shown in Figure 1.1a.

Example 1: Into an apparatus in accordance with Figure 1.1a is introduced by way of the first inlet 13, a 20% solution of phosgene in ortho-dichlorobenzene at a rate of about 130 gallons per minute. This solution continually passes up through the grooves 17 in the rotor 3 which is continually rotated at a rate of 840 rpm. The rotor 3 has a diameter of about 12", a length of about 30" and has 20 lands 15 and 20 grooves 17. The grooves 17 are 1/8" deep and 1.4" wide. The lands 15 are approximately 1/2" wide.

A 20% solution of an isomeric mixture of tolylene diamine approximately 80% 2,4- and 20% 2,6- in an ortho-dichlorobenzene is introduced at a rate of 48 gallons per minute into the grooves 17 through the second inlet 19. This inlet includes 24 holes 21 through the chamber wall 5 equally spaced around the circumference thereof. As the rotor 3 rotates and the grooves 17 become aligned with the holes 21, the tolylene diamine solution enters and mixes with the phosgene solution. Thus, it can be seen that 6,720 separate introductions of tolylene diamine solution are made per second.

$$(840 \text{ rpm} \div 60 \text{ seconds}) (24 \text{ holes}) (20 \text{ ribs}) = 6,720 \text{ introductions per second}$$

The phosgene solution is maintained at a temperature of about 20°C. and is introduced at a pressure of about 125 psig. The tolylene diamine solution is maintained at a temperature of about 80°C. and is introduced at a pressure of about 75 psig. The temperature within the grooves 17 is about 50° to 70°C. The residence time within the grooves 17 under these conditions is about 0.15 second.

The time required to disperse the TDA solution is on the order of 0.004 second. The TDA solution per introduction amounts to about 0.52 g. While the DA solution is shut off, the amount of phosgene solution which flows as a flush amounts to about 0.51 g. The peripheral speed at 840 rpm is 44 feet per second and the upward flow velocity in the channels is 16 feet per second.

The discrete reaction mixtures are collected in the area and pass continuously into another vessel at atmospheric pressure having a stirrer where the reaction mixture is heated to a temperature of about 150°C. for a residence time of about 2 hours while adding phosgene. Excess phosgene and HCl are removed and the solvent is recovered from the product by distillation. The product is purified by further distillation. The method of phosgenation described in this example results in a yield of tolylene diisocyanate of about 94% of theoretical.

Example 2: Into an apparatus in accordance with Figure 1.1d is introduced, by way of the first inlet 13, a 20% solution of phosgene in ortho-dichlorobenzene at a rate of about 130 gallons per minute. This solution flows in high velocity jet streams out of the 20 holes 59 in the rotor. A 20% solution of tolylene diamine in ortho-dichlorobenzene is introduced at a rate of 48 gallons per minute through the 24 holes 21. The amine solution from the stationary holes 21 meets the phosgene solution from the rotating holes 59. The two streams mix and flow together up the vertical grooves 17 and out as in Example 1. In this example, the amine solution and phosgene solution are brought together in a mixing chamber 1/2" x 1/4" x the

circumference of the rotor. The residence time in the mixing chamber is 0.007 second and in the vertical channels is 0.15 second. The velocity of amine solution through the holes is 30 feet per second. The phosgene solution has a radial and opposing velocity of 30 feet per second plus a peripheral speed of 44 feet per second. The amine solution cannot escape from the mixing chamber until it reaches the peripheral speed of the grooves of 44 feet per second. Thus, the flow entering the vertical grooves is almost certain to be homogeneous. The method of phosgenation described in this example results in a yield of tolylene diisocyanate slightly lower than in Example 1.

Example 3: In this example, the apparatus is modified to give different conditions of mixing and reacting, but the flow rates, concentrations and temperatures are the same as in Example 1. In accordance with Figure 1.1e, the phosgene solution enters at nozzle 13 and flows into a space below the rotor and flows at high velocity through 20 holes 59 in the rotor. Lands 15 are provided on either side of each hole 59 to form 20 mixing compartments 17.

The amine solution enters at nozzle 19 and flows at high velocity through 24 holes and then into the 20 mixing compartments. The amine solution flow is a pulsing flow such that there are 6,720 introductions of amine solution in accord with each introduction followed by a phosgene solution flush. The flows leaving the mixing compartments 17 enter the reaction where they combine and spiral upward through an annular space where most of the reaction takes place in a residence time of 0.35 second. This method results in a yield of tolylene diisocyanate slightly lower than Example 1.

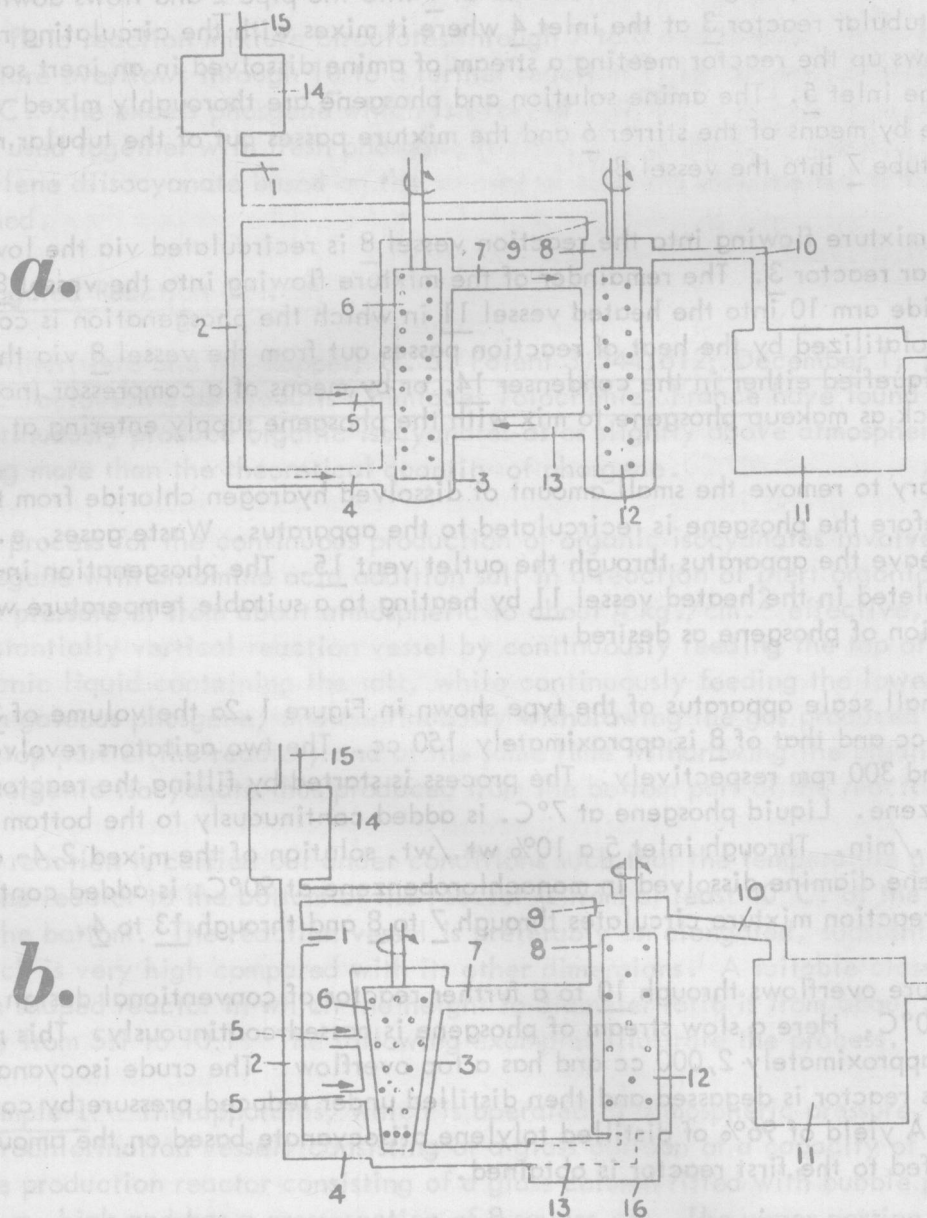
Tubular Reactor

A.J. Nicholas and H.J. Twitchett; U.S. Patent 3,465,021; September 2, 1969; assigned to Imperial Chemical Industries Limited, England describe a process for the production of organic isocyanates which includes reacting phosgene with a primary amine in the presence of an inert organic diluent.

The initial chemical combination of these reactants is performed by separately introducing liquid phosgene and a solution of the primary amine in an inert liquid organic diluent into a tubular reactor through which a stream of a mixture in the same inert organic liquid diluent of phosgene, and the initial reaction products resulting from interaction of phosgene and primary amine is passing continuously by recirculation. The temperature in the reactor is maintained at about 8° to 50°C. and phosgene is added to the recirculating stream of the mixture in amounts of 5 to 20 mols of phosgene per mol of amino group present in the primary amine.

Diagrammatic sketches of suitable forms of apparatus for carrying out the process are shown in the accompanying Figures 1.2a and 1.2b. Referring to Figure 1.2a the apparatus comprises a tubular reactor 3 and a vessel 8 connected together by two tubes, an upper tube 7 and a lower tube 13. The tubular reactor 3 and the vessel 8 are both provided with stirrers 6 and 12 respectively. The tubular reactor 3 is also provided with an inlet 5 for the introduction of amine solution and with an inlet 4 for liquid phosgene connected by a pipe 2 with a source of phosgene at 1, and a condenser 14 carrying an outlet vent 15. The vessel 8 carries a vent tube 9 connected to the pipe 2 and thus to the condenser 14. The vessel 8 is also provided with a side arm 10 which connects with a further heated vessel 11 in which

FIGURE 1.2: TUBULAR REACTOR PROCESS FOR AROMATIC ISOCYANATES



Source: A. J. Nicholas and H. J. Twitchett; U.S. Patent 3,465,021; September 2, 1969

the phosgenation is completed. The apparatus shown in Figure 1.2b is similar to that of Figure 1.2a with minor modifications: Thus, in Figure 1.2b the reactor 3 is not cylindrical but is in the shape of an inverted conic frustum and carries two inlets 5 for the introduction of amine solution, additionally the lower tube 13 connecting the reactor 3 and the reaction vessel 8 is partially surrounded by a cooling jacket 16 where it leaves the vessel 8.

When the apparatus is in use phosgene is introduced at 1 into the pipe 2 and flows down the pipe 2 to enter the tubular reactor 3 at the inlet 4 where it mixes with the circulating reaction mixture and flows up the reactor meeting a stream of amine dissolved in an inert solvent and introduced at the inlet 5. The amine solution and phosgene are thoroughly mixed with the reaction mixture by means of the stirrer 6 and the mixture passes out of the tubular reactor 3 via the upper tube 7 into the vessel 8.

A proportion of the mixture flowing into the reaction vessel 8 is recirculated via the lower tube 13 to the tubular reactor 3. The remainder of the mixture flowing into the vessel 8 passes through the side arm 10 into the heated vessel 11 in which the phosgenation is completed. Phosgene volatilized by the heat of reaction passes out from the vessel 8 via the vent tube 9 and is liquefied either in the condenser 14, or by means of a compressor (not shown) and flows back as makeup phosgene to mix with the phosgene supply entering at 1.

It is found unnecessary to remove the small amount of dissolved hydrogen chloride from the makeup phosgene before the phosgene is recirculated to the apparatus. Waste gases, e.g., hydrogen chloride leave the apparatus through the outlet vent 15. The phosgenation involved may be completed in the heated vessel 11 by heating to a suitable temperature with or without the addition of phosgene as desired.

Example 1: In a small scale apparatus of the type shown in Figure 1.2a the volume of 3 is approximately 50 cc and that of 8 is approximately 150 cc. The two agitators revolve at the rate of 600 and 300 rpm respectively. The process is started by filling the reactor with monochlorobenzene. Liquid phosgene at 7°C. is added continuously to the bottom of 3 at the rate of 12 g./min. Through inlet 5 a 10% wt./wt. solution of the mixed 2,4- and 2,6-isomers of tolylene diamine dissolved in monochlorobenzene at 90°C. is added continuously. The liquid reaction mixture circulates through 7 to 8 and through 13 to 4.

Excess reaction mixture overflows through 10 to a further reactor of conventional design (11) maintained at 90°C. Here a slow stream of phosgene is passed continuously. This reactor has a volume of approximately 2,000 cc and has a top overflow. The crude isocyanate which flows from this reactor is degassed and then distilled under reduced pressure by conventional methods. A yield of 96% of distilled tolylene diisocyanate based on the amount of tolylene diamine fed to the first reactor is obtained.

Example 2: The tolylene diamine solution of Example 1 is replaced by an 8% wt./wt. solution of the mixed 2,4- and 2,6-isomers of tolylene diamine dissolved in ortho-dichlorobenzene, the remaining conditions being the same. A yield of 98.2% of distilled tolylene diisocyanate based on the amount of tolylene diamine fed to the first reactor is obtained.

Example 3: This is carried out in the apparatus used in Example 1. The agitator in the tubular reactor 3 operates at 100 rpm and that in vessel 8 at 300 rpm. The process is started