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(54) **Titre :** PREPARATION CONTINUE EN PLUSIEURS ETAPES DE DIISOCYANATES CYCLOALIPHATIQUES
(54) **Title:** MULTISTAGE CONTINUOUS PERPARATION OF CYCLOALPHATIC DIISOCYANATES

(57) **Abrégé/Abstract:**
Disclosed is a multistage process for continuous and phosgene-free preparation of a cycloaliphatic diisocyanate. The process comprises (A) reacting a cycloaliphatic diamine with urea to form cycloalkylenebisurea, (B) reacting the cycloalkylenebisurea with an alcohol to form a cycloalkylenediurethane, (C) removing high- and medium-boiling components (e. g. alcohol) from the cycloalkylenediurethane without removing high-boiling residues, (D) thermally cleaving the cycloalkylenediurethane to obtain the cycloaliphatic diisocyanate, while discharging a portion of the uncleaved cycloalkylenediurethane, (E) reurethanizing the discharged portion with the alcohol, (F) removing the high-boiling residues from the reurethanized product; and (G) recycling the purified reurethanized product. By adopting a two-stage reaction (A and B) to form the diurethane, the method realizes a low steady-state concentration of the high-boiling residues that are viscous and tend to form deposits.

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Abstract:

Disclosed is a multistage process for continuous and phosgene-free preparation of a cycloaliphatic diisocyanate. The process comprises (A) reacting a cycloaliphatic diamine with urea to form cycloalkylenebisurea, (B) reacting the cycloalkylenebisurea with an alcohol to form a cycloalkylenediurethane, (C) removing high- and medium-boiling components (e.g. alcohol) from the cycloalkylenediurethane without removing high-boiling residues, (D) thermally cleaving the cycloalkylenediurethane to obtain the cycloaliphatic diisocyanate, while discharging a portion of the uncleaved cycloalkylenediurethane, (E) reurethanizing the discharged portion with the alcohol, (F) removing the high-boiling residues from the reurethanized product; and (G) recycling the purified reurethanized product. By adopting a two-stage reaction (A and B) to form the diurethane, the method realizes a low steady-state concentration of the high-boiling residues that are viscous and tend to form deposits.

Multistage continuous preparation of cycloaliphatic diisocyanates

The invention relates to a multistage process for continuous and phosgene-free preparation of cycloaliphatic diisocyanates.

The synthetic access route to isocyanates may be via a series of different routes. The variant for industrial scale preparation of isocyanates which is the oldest and still predominates today is what is known as the phosgene route. This process is based on the reaction of amines with phosgene. A disadvantage of the phosgene process is the use of phosgene which, as a consequence of its toxicity and corrosivity, places particularly high requirements on its handling on the industrial scale.

There are several processes which avoid the use of phosgene for preparing isocyanates on the industrial scale. The term phosgene-free process is frequently used in connection with the conversion of amines to isocyanates using alternative carbonylating agents, for example urea or dialkyl carbonate (EP 018 586, EP 355 443, US 4,268,683, EP 990 644).

The urea route is based on the urea-mediated conversion of diamines to diisocyanates via a two-stage process. In the first step, a diamine is reacted with alcohol in the presence of urea or urea equivalents (for example alkyl carbonates, alkyl carbamates) to give a diurethane which typically passes through an intermediate purification stage and is then thermally cleaved in the second step to diisocyanate and alcohol (EP 355 443, US 4,713,476, US 5,386,053). Alternatively, the actual urethane formation may also be preceded by the separate preparation of a diurea by selectively reacting the diamine with urea (EP 568 782). Also conceivable is a two-stage sequence consisting of partial reaction of urea with alcohol in the first and subsequent metering in and urethanization of the diamine in the second step (EP 657 420).

The thermal cleavage of urethanes to the corresponding isocyanates and alcohols has been known for some time and can be carried out either in the gas phase at high temperatures or at relatively low temperatures in the liquid phase. However, a problem in both procedures is that the thermal stress inevitably also causes undesired side reactions to take place which firstly reduce the yield and secondly lead to the formation of resinifying by-products which considerably disrupt the course of an industrial process as a result of deposits and blockages in reactors and workup apparatus.

There has therefore been no shortage of suggestions of chemical and process technology measures to achieve yield improvements and limit the undesired by-product formation. For instance, a series of documents describes the use of catalysts which accelerate the cleavage reaction of the urethanes (DE 10 22 222, US 3,919,279, DE 26 35 490). Indeed, it is entirely possible in the presence of suitable catalysts, which are a multitude of basic, acidic and also organometallic compounds, to increase the isocyanate yield in comparison to the uncatalyzed variant. However, the formation of undesired by-products can also not be prevented by the presence of a catalyst. The same applies to the additional use of inert solvents, as recommended in US 3,919,279 and DE 26 35 490, in order to ensure uniform distribution of the heat supplied and of the catalyst in the reaction medium. However, the use of solvents boiling under reflux fundamentally has the consequence of a reduction in the space-time yield of isocyanates and is additionally hindered with the disadvantage of additional high energy demands.

Examples which are cited in EP 054 817 for thermal catalyzed cleavage of monourethanes describe the partial discharge of the reaction mixture to remove resinifying by-products formed in the course of the urethane cleavage. This procedure serves to prevent deposits and blockages in reactors and workup units. There are no indications which point to a yield-increasing utilization of the partial discharge. EP 61 013 describes a similar approach to a solution, in which the thermolysis is in this case carried out in the presence of solvents whose purpose is apparently to better absorb the involatile by-products. Here also, the partial discharge is not utilized for the purposes of yield optimization.

EP 355 443 discloses that a yield increase can be achieved when the higher molecular weight by-products which can and cannot be utilized and are formed in the cleavage reactor during the cleavage of diurethanes, to ensure a disruption-free and selective reaction, are discharged substantially continuously out of the reactor and subsequently converted for the most part in the presence of alcohol and then recycled into the diurethane preparation. The procedure described is associated with high energy demands, since nonutilizable by-products are removed from the effluent of the diurethane preparation by distillation, and all of the diurethane has to be evaporated. In contrast to EP 355 443, the urethanization effluent in the process of EP 566 925 is divided into two substreams of which only one is freed by distillation of its high-boiling, nonutilizable by-products, before the combined diurethane streams are fed to the deblocking reaction in the cleavage reactor. In addition, the continuous cleavage reactor discharge in EP 566 925 is recycled directly, i.e. without a reurethanization step, into the diurethane synthesis.

The preparation of the diurethanes in a one-pot reaction from urea, diamine and alcohol with simultaneous removal of ammonia is common practice and is described in a series of patents (EP 018 568, EP 355 443, EP 566 925). A disadvantage is that the simultaneous reaction of urea, alcohol and diamine inevitably forms by-products in a relatively large amount, which impair the selectivity of the reaction and which have to be removed before the thermal deblocking of the diurethanes. EP 568 782 therefore claims a continuous process for preparing (cyclo)aliphatic diisocyanates which comprises essentially three main steps, of which the first describes the formation of bisureas, the second the formation of diurethanes from the bisureas and the third the cleavage of the diurethanes in the liquid phse to the desired diisocyanates - i.e. the diurethane is prepared in two separate stages. According to the teaching of EP 568 782, the effluent of the reaction sequence from bisurea formation and subsequent diurethane synthesis is initially freed distillatively of low and medium boilers such as alcohols, carbamates and carbonates, and the high boilers in the diurethane are removed afterward by short-path evaporation. The diurethane is deblocked thermally and a portion of the cleavage residue is discharged continuously, reurethanized with alcohol and recycled back into the diurethane synthesis stage.

It has been found that, surprisingly, when cycloaliphatic diamines are used, it is advantageous to prepare the cycloaliphatic diamines by two-stage reaction, which thus proceeds via bisurea, of cycloaliphatic diamines with alcohol and urea, to free them, to thermally cleave the cycloaliphatic diurethanes purified in this way to release the desired cycloaliphatic diisocyanate, to continuously discharge a portion of a cleavage residue from a cleavage apparatus and to reurethanize with alcohol to remove high boiler components therefrom, and to recycle a reurethanized stream purified in this way into the process. It has been found that this method firstly realizes a comparatively low steady-state concentration of high boiler components over the entire sequence of diurethane synthesis, diurethane purification and diurethane cleavage, so that deposits, which are promoted in particular by the high boiler components which are highly viscous by nature, can be substantially avoided, and also ensures good plant availability and good process yield even in the long term. Secondly, the sequence of reurethanization and high boiler removal downstream of the thermal cleavage reaction has the advantage that, in comparison to the customary procedure in which the high boilers are removed before the diurethane cleavage, the amount of diurethane to be converted to the vapor phase is significantly reduced, which allows capital and energy costs to be reduced.

The invention provides a multistage process for continuously preparing a cycloaliphatic diisocyanate of the formula:

$$OCN\text{-}R\text{-}NCO$$

(wherein R is a bivalent cycloaliphatic radical having 4 to 18 carbon atoms),

which comprises:

(A) reacting a cycloaliphatic diamine of the formula:

$$H_2N\text{-}R\text{-}NH_2$$

(wherein R is as defined above)

with urea, while removing formed ammonia, to obtain a cycloalkylenebisurea of the formula:

$$H_2N\text{-}OC\text{-}HN\text{-}R\text{-}NH\text{-}CO\text{-}NH_2$$

(wherein R is as defined above);

(B) reacting the cycloalkylenebisurea with an alcohol of the formula:

$$R^1\text{-}OH$$

(wherein R^1 is a primary or secondary aliphatic or cycloaliphatic hydrocarbon radical having 1 to 8 carbon atoms),

while removing formed ammonia, to obtain a cycloalkylenediurethane of the formula:

$$R^1\text{-}O\text{-}OC\text{-}HN\text{-}R\text{-}NH\text{-}CO\text{-}OR^1$$

(wherein R and R^1 are as defined above),

in a reaction mixture which also contains the alcohol and high-boiling residues and may further contain a dialkyl carbonate $R^1\text{-}O\text{-}CO\text{-}O\text{-}R^1$ and/or an alkyl carbamate $R^1\text{-}O\text{-}CO\text{-}NH_2$;

(C) removing the alcohol, and where present, the dialkyl carbonate and/or the alkyl carbamate from the reaction mixture, to obtain a purified reaction mixture containing the cycloalkylenediurethane and the high-boiling residues;

(D) subjecting the purified reaction mixture to a thermal cleavage in a cleavage apparatus, to obtain the cycloaliphatic diisocyanate, while continuously discharging a portion of the purified mixture from a bottom of the cleavage apparatus;

(E) reurethanizing the discharged portion of the purified mixture by a reaction with the alcohol, to obtain a reurethanization product;

(F) removing the high-boiling residues from the reurethanization product; and

(G) recycling the reurethanization product from which the high-boiling residues have been removed, into the process.

The invention in a preferred embodiment provides a multistage process for continuously preparing a cycloaliphatic diisocyanate of the formula (I):

$$OCN\text{-}R\text{-}NCO \qquad (I)$$

(where R is a bivalent cycloaliphatic hydrocarbon radical having from 4 to 18, preferably from 5 to 15, carbon atoms, with the proviso that the two N atoms are bonded directly to a hydrocarbon cycle and at least 3 carbon atoms are disposed between them), wherein:

a) a cycloaliphatic diamine of the formula (II):

$$H_2N\text{-}R\text{-}NH_2 \qquad (II)$$

(where R is as defined above) is reacted in a first reactor with urea in the presence of, as a solvent, a primary or secondary (cyclo)aliphatic alcohol having from 1 to 8 carbon atoms of the formula (III):

$$R^1\text{-}OH \qquad (III),$$

in the absence or presence of a catalyst to give a cycloalkylenebisurea of the formula (IV):

$$H_2N\text{-}OC\text{-}HN\text{-}R\text{-}NH\text{-}CO\text{-}NH_2 \qquad (IV)$$

(where R is as defined above), while ammonia which is formed is removed simultaneously;

b) the resulting crude cycloalkylenebisurea is converted in a second reactor using the alcohol of the formula (III) used as a solvent in a), while continuously driving out ammonia released, to a cycloalkylenediurethane of the formula (V):

$$R^1O\text{-}OC\text{-}HN\text{-}R\text{-}NH\text{-}CO\text{-}OR^1 \qquad (V)$$

in a reaction mixture which contains the alcohol, a dialkyl carbonate ($R^1\text{-}O\text{-}CO\text{-}OR^1$) and/or an alkyl carbamate ($R^1\text{-}O\text{-}CO\text{-}NH_2$);

c) the alcohol, the dialkyl carbonate and/or alkyl carbamate are removed from the resulting reaction mixture and the alcohol is recycled to reaction stage a);

d) optionally high-boiling residues present in the resulting reaction mixture are removed;

e) the reaction mixture comprising the diurethane of the formula (V) purified by step c) alone or in combination with step d) is thermally cleaved in the presence of a catalyst continuously and without solvent, at a temperature of from 180 to 280°C, preferably from 200 to 260°C, and under a pressure of from 0.1 to 200 mbar, preferably from 0.2 to 100 mbar, in such a way that a portion (i.e., 10 to 60%, preferably 15 to 45% by weight) of the reaction mixture is constantly discharged from a bottom;

f) the cleavage products are separated by rectification into crude diisocyanate of the formula (I) and the alcohol of formula (III);

g) the crude cycloaliphatic diisocyanate is purified by distillation, and a pure product fraction of the diisocyanate is isolated;

h) a bottoms discharge from e) is reacted partially or fully with the alcohol from f) in the presence or absence of a catalyst, preferably for 1 to 150 min, more preferably from 3 to 60 min, at an appropriate temperature, e.g., from 20 to 200°C, more preferably 50 to 170°C, and at an appropriate pressure, e.g., 0.5 to 20 bar, more preferably from 1 to 15 bar, at a preferred molar ratio of NCO groups to OH groups of from 1:1 to 1:100, more preferably 1:1 to 1:20 and particularly preferably 1:1 to 1:10;

i) a stream from h) is separated into a material-of-value stream and a waste stream, and the waste stream which is rich in high boiler components is discharged from the process and disposed of;

j) a portion of the bottoms fraction of the purification by distillation g) is continuously discharged and conducted into the cleavage reaction e) or into the urethanization stage h);

k) optionally, a top fraction obtained in the purification distillation of the crude cycloaliphatic diisocyanate is likewise recycled into the urethanization stage h); and

l) the purified reurethanized stream from i) is recycled into at least one of stages b), c) and e).

In the process according to the invention, cycloaliphatic diisocyanates can be prepared continuously, without any problem and in a very good yield. What is advantageous in the multistage process according to the invention is in particular the fact that even when cycloaliphatic diamines of the formula (II) are used as a starting material for the continuous diisocyanate synthesis, deposits, which are supported in particular by the high boiler components which are highly viscous by nature, can be substantially prevented and good plant availability and good process yield are ensured even in the long term. It is a further advantage of the multistage process according to the invention that it allows the amount of the diurethane to be converted to the vapor phase to be reduced to a minimum and in this way restricts the necessary energy demands.

a) To prepare the cycloalkylenebisureas of the formula (IV) in reaction stage a), the cycloaliphatic diamines of the formula (II) are reacted with urea in the presence of an alcohol of the formula (III), if desired also mixtures of such alcohols, desirably at from 100 to 145°C and a pressure of from 0.7 to 1.8 bar, in the course of which the ammonia formed is driven out continuously. The reaction is effected preferably in a distillation reactor, in which case the reactants are introduced in a molar ratio of diamine : urea : alcohol of 1 : 2.0 to 2.4 : 3 to 10 continuously to the uppermost tray and the ammonia released is driven out by alcohol vapours which are introduced in the bottom of the distillation reactor. The required residence time is from 4 to 10 hours, preferably from 5 to 9 hours. The amount of alcohol introduced in the bottom to drive out the ammonia is from 0.05 to 3 kg/kg, preferably from 0.1 to 1 kg/kg, of bisurea, and the amount of alcohol thus introduced is drawn off at the top together with ammonia formed, freed of residual ammonia after partial condensation in an alcohol recovery column, and recycled into the bottom.

b) The crude cycloalkylenebisurea dissolved in alcohol which is obtained in the bottom of the distillation reactor is conducted continuously into a second reactor in which the conversion to the diurethane is effected at elevated temperature and elevated pressure, in the course of which ammonia is again released, and has to be removed from the reaction mixture for reasons of chemical equilibrium. The crude cycloalkyleneurea from a) is reacted further preferably in a pressure distillation reactor and at a molar ratio of bisurea to alcohol of from 1 : 5 to 12. The stream from a) is conducted preferably continuously to the uppermost tray of the pressure distillation reactor. The reaction takes place in the absence or presence of catalysts at reaction temperatures of from 140 to 270°C, preferably from 160 to 250°C, and under a pressure which is from 5 to 20 bar, preferably from 7 to 15 bar, within from 2 to 20 hours, preferably from 8 to 15 hours. The continuous driving-out of the ammonia released is promoted by alcohol vapours which are introduced in the bottom of the pressure distillation reactor and are appropriately generated in an evaporator mounted at the bottom of the column.

To increase the reaction rate, the diurethanes may be prepared in the presence of catalysts. Suitable catalysts are inorganic or organic compounds which contain one or more, preferably a cation of, metals or groups IA, IB, IIA, IIB, IIIA, IIIB, IVA, IVB, VA, VB, VIB, VIIB and VIIIB of the Periodic Table, defined in accordance with Handbook of Chemistry and Physics 14th Edition, published by Chemical Rubber Publishing Co. 2310 Superior Ave. N.E. Cleveland, Ohio, for example halides such as chlorides and bromides, sulfates, phosphates, nitrates, borates, alkoxides, phenoxides, sulfonates, oxides, oxide hydrates, hydroxides, carboxylates, chelates, carbonates and thio- or dithiocarbamates. Examples include the cations of the following metals: lithium, sodium, potassium, magnesium, calcium, aluminum, gallium, tin, lead, bismuth, antimony, copper, silver, gold, zinc, mercury, cerium, titanium, vanadium, chromium, molybdenum, manganese, iron, cobalt and nickel. Examples of typical catalysts include the following compounds: lithium ethoxide, lithium butoxide, sodium methoxide, potassium tert-butoxide, magnesium ethoxide, calcium methoxide, tin(II) chloride, tin(IV) chloride, lead acetate, aluminum trichloride, bismuth trichloride, copper(II) acetate, copper(II) chloride, zinc chloride, zinc octoate, titanium tetrabutoxide, vanadium trichloride, vanadium acetylacetonate, manganese(II) acetate, iron(II) acetate, iron(III) acetate, iron oxalate, cobalt chloride, cobalt naphthenate, nickel chloride, nickel naphthenate and mixtures thereof. The catalysts may optionally also be used in the form of their hydrates or ammoniates.

Starting compounds for the process according to the invention are diamines of the formula (II) which has already been mentioned above, alcohols of the formula (III) which has already been mentioned above, and also urea. Suitable diamines of the formula (II) are, for example, 1,4-diaminocyclohexane, 4,4‘-dicyclohexylmethanediamine, 2,4-dicyclohexylmethanediamine, 2,2‘-dicyclohexylmethanediamine and isomeric cycloaliphatic diamines, and also perhydrogenated diphenylmethanediamine. As a result of the preparation, diphenylmethanediamine (MDA) occurs as an isomer mixture of 4,4‘-, 2,4- and 2,2‘-MDA (see, for example, DE 101 27 273). Perhydrogenated diphenylmethanediamine is obtained by fully hydrogenating MDA and is accordingly a mixture of isomeric dicyclohexylmethanediamines (H_{12}MDA), i.e. 4,4‘-, 2,4- and 2,2‘-H_{12}MDA and possibly small amounts of (semi)aromatic MDA which has not been fully converted. The diamines of the formula (II) used are preferably 4,4‘-dicyclohexylmethanediamine, 2,4-dicyclohexylmethanediamine and 2,2‘-dicyclohexylmethanediamine, and also any mixtures of at least two of these isomers. It will be appreciated that diamines may also be used which deviate from the formula (II). Examples include 1,3- and 1,4-diaminomethylcyclohexane, 1,6-hexanediamine, 2,2,4- or 2,4,4-trimethyl-1,6-hexanamine and 3-aminomethyl-3,5,5-trimethylcyclohexylamine. However, preference is not given to using amines which deviate from the formula (II).

Suitable alcohols of the formula (III) are any aliphatic or cycloaliphatic alcohols which have a boiling point below 190°C under atmospheric pressure. Examples include C1-C6-alkanols, for example methanol, ethanol, 1-propanol, 1-butanol, 2-butanol, 1-hexanol or cyclohexanol. The alcohol used is preferably 1-butanol.

In the course of the conversion of the reaction mixture, ammonia is released, whose removal from the reaction equilibrium has been found to be advantageous. When ammonia is discharged from the reactor, care has to be taken that the wall temperatures of the reactor and of the discharge tube are above 60°C, so that deposition of ammonium carbamate, which is formed in minimal amounts from ammonia and carbon dioxide by decomposition of urea, can be prevented. It has been found to be useful, for example, to carry out the reaction in a pressure distillation reactor, in which case the reaction mixture is conducted in countercurrent to alcohol vapors introduced in the bottom and in this way such intensive mixing of the liquid proceeds on the trays that they each virtually correspond to a battery stage. The vaporous mixture of alcohol and ammonia which is withdrawn at the top may, preferably under the pressure of the pressure distillation reactor and without condensing it beforehand, be conducted into a distillation column, to obtain alcohol free from ammonia. The alcohol is recycled into the bottom of the pressure distillation reactor and of the column. In order to prevent fouling of the reflux condenser with ammonium carbamate, an appropriate proportion of alcohol is permitted therein to set the temperature at the top to at least 60°C.

c) The excess alcohol, the dialkyl carbonates, if they have been formed, or alkyl carbamates or mixtures of at least two of these components are removed in one stage or advantageously in two stages. At the first stage, the reaction mixture is decompressed from the pressure level of reaction stage b) to a pressure of from 1 to 500 mbar, preferably from 2 to 150 mbar, and in this way separated into gaseous vapors which contain the predominant amount of alcohol and also any dialkyl carbonates and/or alkyl carbamates, and into a liquid effluent. In the second stage, the liquid effluent is freed of any remaining residual butanol and also medium boilers such as dialkyl carbonates and/or alkyl carbamates by thin-film evaporation at from 180 to 250°C, preferably from 200 to 230°C, and a pressure of from 0.1 to 20 mbar, preferably from 1 to 10 mbar, so that the residue consists substantially of the monomeric diurethane and in some cases high-boiling oligomers. The vapors may, after further distillative purification, be recycled into reaction stage a). Recycling of the dialkyl carbonates and/or alkyl carbamates into reaction stage b) is possible but not necessary.

d) Preference is given to dispensing with any removal of any high boilers present in the reaction mixture from stage c). However, if the separation described under i) of the reurethanized stream from stage h) is carried out only with one substream, i.e. partially, it may be advantageous to follow the routes for high boiler removal which are described below:

Optionally, the liquid stream from step c) which contains the monomeric diurethanes and any high-boiling oligomers and is obtained after the removal of low and medium boilers may be separated, preferably with the aid of a thin-film or short-path evaporator, at a temperature of from 180 to 270°C, preferably from 200 to 250°C, and under a pressure of from 0.01 to 10 mbar, preferably from 0.02 to 5 mbar, by distillation into a material-of-value stream which contains the monomeric diurethanes and the lower-boiling by-products and a nondistillable by-product stream. The nondistillable by-product stream which contains the high-boiling components is discharged from the preparative process and is typically discarded as a residue whose material cannot be utilized.

Optionally, the stream from stage c) which contains any high-boiling oligomers, before its above-described distillative purification, may also be divided into two substreams of which one is fed directly to the deblocking reaction (see e)) and the other initially passes through the high boiler removal just described.

e) The material-of-value stream from stage c) and optionally from stage d) which contains the monomeric diurethanes and the lower-boiling by-products is partly and continuously thermally cleaved in a suitable apparatus, without solvents in the liquid phase in the presence of catalysts at temperatures of from 180 to 280°C, preferably from 200 to 260°C, and under a pressure of from 0.1 to 200 mbar, preferably from 0.2 to 100 mbar. The conversion of diurethane to diisocyanate in the apparatus for thermal cleavage may, depending on the diurethane used, be selected substantially freely and is typically within the range of from 10 to 95% by weight, preferably from 35 to 85% by weight of the diurethane feed. The uncleaved proportion of the reaction mixture which contains unconverted diurethanes, high-boiling by-products and other reutilizable and nonutilizable by-products is continuously discharged. The amount of the discharge is governed, inter alia, by the desired conversion and the desired capacity of the cleavage reaction and can be easily determined experimentally. It is typically from 10 to 60% by weight, preferably from 15 to 45% by weight, based on the feed.

Useful catalysts for chemically cleaving the diurethanes are, for example, the aforementioned inorganic and organic compounds which catalyze urethane formation. Preference is given to using chlorides of zinc, tin, or copper, and also zinc oxides, manganese oxides, iron oxides or cobalt oxides, in which case the catalyst is metered into the stream from the purification stage c) and optionally d), before it is fed into the cleavage, as a from 0.01 to 25% by weight, preferably from 0.05 to 10% by weight, solution or suspension, preferably into the alcohol which is also used for urethane preparation, in an amount of from 5 to 400 ppm, preferably from 10 to 100 ppm.

Suitable cleavage apparatus is, for example, cylindrical cleavage reactors, for example tubular furnaces or preferably evaporators such as falling-film, thin-film or bulk evaporators, selected from Robert evaporators, Herbert evaporators, Caddle-type evaporators, Oskar evaporators and heating cartridge evaporators.

In principle, the main concern is to keep the average residence time of isocyanate groups, which are inevitably released when the alcohol is deblocked, in the cleavage zone very low and thus to limit undesired side reactions to a minimum.

Preference is given to carrying out the cleavage in a combined cleavage and rectification column, which is equipped for the energy supply in the bottom with a falling-film evaporator, in the lower third with a unit for additional energy input or for energy recovery, in the upper third with a unit to remove preferably crude diisocyanate and at the top with a condenser for the reflux and the removal of pure alcohol.

f) The cleavage products which are formed in the thermal cleavage and are composed in particular of alcohol, diisocyanate and partially cleaved diurethanes are separated by rectification at from 95 to 260°C, preferably from 110 to 245°C, and a pressure of from 0.5 to 250 mbar, preferably from 1 to 100 mbar, into alcohol and into a crude diisocyanate mixture, consisting of cycloaliphatic diisocyanate, partially cleaved cycloaliphatic diisocyanate and in some cases small amounts of cycloaliphatic diurethane. This separation may be carried out, for example, in the cleavage column of the abovementioned combined cleavage and rectification column.

g) The crude mixture which is preferably obtained by rectification, consisting of cycloaliphatic diisocyanate, partially cleaved cycloaliphatic diurethane and in some cases small fractions of cycloaliphatic diurethane, is purified by distillation at a temperature of from 95 to 260°C, preferably from 110 to 245°C, and under a pressure of from 0.5 to 150 mbar, preferably from 1 to 75 mbar, and the resulting fractions are recycled or isolated as a pure product.

h) The bottoms discharge from the deblocking stage e) is recycled partially or fully with the alcohol from the rectification stage f), the molar ratio of NCO groups to OH groups being up to 1:100, preferably 1:20 and more preferably 1:10, and the reaction mixture is reacted in the presence or absence of catalysts, within from 1 to 150 min, preferably from 3 to 60 min, at temperatures of from 20 to 200°C, preferably from 50 to 170°C and a pressure of from 0.5 to 20 bar, preferably from 1 to 15 bar. The reaction may be carried out in a continuous tank battery or in a tubular reactor. Useful catalysts are in principle any catalysts which promote the NCO/OH reaction. Examples include tin octoate, dibutyltin laurate, tin dichloride, zinc dichloride, copper chloride, copper dichloride, iron dichloride, iron trichloride and triethylamine.

i) The reurethanized stream from stage h) is separated into a material-of-value and a waste stream and the waste stream rich in high boiler components is discharged from the process and discarded. The two streams are separated preferably by distillation with the aid of a thin-film or short-path evaporator, at a temperature of from 180 to 270°C, preferably from 200 to 250°C, and under a pressure of from 0.01 to 10 mbar, preferably from 0.02 to 5 mbar. The material-of-value stream which comprises the monomeric diurethanes and the lower-boiling by-products is obtained as the distillate. The waste stream which is rich in high-boiling components is obtained as the residue and is discharged from the preparative process and typically discarded as a nonutilizable material. Alternatively, but not preferably, the separation into material-of-value and waste material may also be effected by extraction. An example of a suitable extractant is supercritical carbon dioxide.

Optionally, the reurethanized stream may also be divided into two substreams before the distillative purification described above, from which one is fed directly to the purification stage c). The two streams can be divided in a ratio of from 99:1 to 1:99, preferably from 99:5

to 5:95. Optionally, the reurethanized stream leading to the high boiler removal may initially be freed partly or fully of excess alcohol. This is preferably effected by distillation. The alcohol removed may be recycled as desired in stage a) and/or b).

j) A portion of the bottoms fraction of the purifying distillation g) is continuously discharged and optionally recycled into the deblocking stage e) or into the urethanization stage h). Preference is given to recycling into the urethanization stage. The amount of the discharge is from 0.1 to 50% by weight, preferably from 0.2 to 25% by weight, of the feed of crude diisocyanate into the purifying distillation stage.

k) The top fraction of the purifying distillation stage g) may be discarded or preferably recycled into the urethanization stage h). The amount of top fraction removed per unit time is from 0.1 to 3% by weight, preferably from 0.3 to 1% by weight, of the feed of crude diisocyanate into the purifying distillation.

l) The purified reurethanized stream from stage i) is recycled into the low and medium boiler removal c) and/or the diurethane preparation b) or the diurethane cleavage c).

The multistage process according to the invention for continuously preparing cycloaliphatic diisocyanates with recycling and discharge of the by-products allows, for distillable cycloaliphatic diisocyanates, a reaction which proceeds without disruption and with high selectivity to be ensured. The process according to the invention is suitable in particular for preparing cycloaliphatic diisocyanates having from 4 to 18, preferably from 5 to 15, carbon atoms, such as 1,4-diisocyanatocyclohexane, 4,4'-dicyclohexylmethane diisocyanate (4,4'-H_{12}MDI), 2,2'-dicyclohexylmethane diisocyanate (2,2'-H_{12}MDI), 2,4-dicyclohexylmethane diisocyanate (2,4-H_{12}MDI) or else mixtures of the aforementioned isomeric dicyclohexylmethane diisocyanates (H_{12}MDI), as are obtained, for example, by the nature of the conversion of perhydrogenated MDA to H_{12}MDI. Very particular preference is given to preparing 4,4'-dicyclohexylmethane diisocyanate, and also any mixtures of 4,4'-H_{12}MDI, 2,4-H_{12}MDI and 2,2'-H_{12}MDI.

The cycloaliphatic diisocyanates prepared are excellently suited to preparing polymers containing urethane, isocyanurate, amide and/or urea groups by the polyisocyanate polyaddition process. They additionally find use for preparing polyisocyanate mixtures modified with urethane, biuret and/or isocyanurate groups. Such polyisocyanate mixtures of cycloaliphatic diisocyanates are used in particular for preparing high-value, light-resistant polyurethane coatings.

The invention is illustrated in detail by the example which follows.

Example

Example 1: Preparation according to the invention of dicyclohexylmethane diisocyanate (H_{12}MDI) from perhydrogenated diphenylmethanediamine and urea in the presence of n-butanol.

Every hour, the uppermost tray of a distillation reactor was charged with 281.5 g of H_{12}MDA, 164.9 g of urea and 595 g of n-butanol, and the reaction mixture was boiled at atmospheric pressure, 135°C and an average residence time of 8 hours while continuously removing the ammonia released. The solution, obtained in the bottom of the distillation reactor, of bisurea in butanol was preheated to 190°C using a heat exchanger, conducted to the uppermost tray of a pressure distillation reactor and reacted further at from 11 to 14 bar, 220°C and with an average residence time of 10.5 h. In the bottom of the pressure distillation reactor, 540.1 g of n-butanol per hour were fed in and the amount of alcohol drawn off at the top together with the ammonia released was selected such that it corresponded to the alcohol introduction in the bottom. The reactor effluent, together with the stream from the high boiler removal, was subsequently freed of excess alcohol, low boilers and medium boilers in the flash vessel at 55 mbar with subsequent thin-film evaporation at 220°C and 2 mbar, and the remaining 771.1 g/h of bis(4-butoxycarbonylaminocyclohexyl)methane (H_{12}MDU) were conducted as a melt (140°C) into the circulation of the falling-film evaporator of the cleavage and rectification column, and the deblocking reaction was carried out at a temperature of 239°C and a bottom pressure of 10 mbar in the presence of a steady-state concentration of tin dichloride of 16 ppm. The cleavage gases, H_{12}MDI and butanol, were condensed out in two condensers connected in series at 85°C and –25°C. The resulting about 97% crude H_{12}MDI was fed to a purifying distillation where 320.9 g/h of H_{12}MDI having a purity of > 99.5% were obtained, which corresponds to a yield based on the amine of 92%. 228.9 g/h of butanol were obtained as the top product of the cleavage and rectification column. To maintain constant mass within the cleavage and rectification column and avoid fouling and blockages of the cleavage apparatus, a substream was continuously discharged from the circuit and, together with 23.7 g/h of bottoms discharge from the H_{12}MDI purifying distillation and the top product from the cleavage and rectification column, purified and reurethanized. The reurethanized stream was freed of excess butanol by flash evaporation at 40 mbar and separated by means of a short-path evaporator at 230°C and a pressure of 0.04 mbar into a waste stream rich in high boilers and a material-of-value stream. The 229.9 g/h of material-of-value stream were fed to the flash vessel together with the reactor effluent of the diurethane preparation.

CLAIMS:

1. A multistage process for continuously preparing a cycloaliphatic diisocyanate of the formula:

OCN-R-NCO

(wherein R is a bivalent cycloaliphatic radical having 4 to 18 carbon atoms),

which comprises:

(A) reacting a cycloaliphatic diamine of the formula:

$H_2N\text{-}R\text{-}NH_2$

(wherein R is as defined above)

with urea, while removing formed ammonia, to obtain a cycloalkylenebisurea of the formula:

$H_2N\text{-}OC\text{-}HN\text{-}R\text{-}NH\text{-}CO\text{-}NH_2$

(wherein R is as defined above);

(B) reacting the cycloalkylenebisurea with an alcohol of the formula:

$R^1\text{-}OH$

(wherein R^1 is a primary or secondary aliphatic or cycloaliphatic hydrocarbon radical having 1 to 8 carbon atoms),

while removing formed ammonia, to obtain a cycloalkylenediurethane of the formula:

$R^1\text{-}O\text{-}OC\text{-}HN\text{-}R\text{-}NH\text{-}CO\text{-}OR^1$

(wherein R and R^1 are as defined above),

in a reaction mixture which also contains the alcohol and high-boiling residues and may further contain a dialkyl carbonate R^1-O-CO-O-R^1 and/or an alkyl carbamate R^1-O-CO-NH_2;

(C) removing the alcohol, and where present, the dialkyl carbonate and/or the alkyl carbamate from the reaction mixture, to obtain a purified reaction mixture containing the cycloalkylenediurethane and the high-boiling residues;

(D) subjecting the purified reaction mixture to a thermal cleavage in a cleavage apparatus, to obtain the cycloaliphatic diisocyanate, while continuously discharging a portion of the purified mixture from a bottom of the cleavage apparatus;

(E) reurethanizing the discharged portion of the purified mixture by a reaction with the alcohol, to obtain a reurethanization product;

(F) removing the high-boiling residues from the reurethanization product; and

(G) recycling the reurethanization product from which the high-boiling residues have been removed, into the process.

2. A multistage process for continuously preparing a cycloaliphatic diisocyanate of the formula (I):

OCN-R-NCO (I)

(where R is a bivalent cycloaliphatic hydrocarbon radical having from 4 to 18 carbon atoms, with the proviso that the two N atoms are bonded directly to a hydrocarbon cycle and at least 3 carbon atoms are disposed between the two N atoms), which comprises:

a) reacting a cycloaliphatic diamine of the formula (II):

$$H_2N\text{-}R\text{-}NH_2 \qquad (II)$$

(where R is as defined above) with urea and in the presence of, as a solvent, a primary or secondary aliphatic or cycloaliphatic alcohol having from 3 to 8 carbon atoms of the formula (III):

$$R^1\text{-}OH \qquad (III)$$

at a temperature of 100 to 145°C and a pressure of 0.7 to 1.8 bar in a first reactor in the absence or presence of a catalyst to give a cycloalkylenebisurea of the formula (IV):

$$H_2N\text{-}OC\text{-}HN\text{-}R\text{-}NH\text{-}CO\text{-}NH_2 \qquad (IV)$$

(wherein R is as defined above), while removing formed ammonia;

b) reacting the resulting cycloalkylenebisurea in a second reactor with the alcohol of the formula (III) at a pressure of 5 to 20 bar and a temperature that is higher than the stage a) and is from 140 to 270°C, while continuously driving out ammonia released, to obtain a cycloalkylenediurethane of the formula (V):

$$R^1O\text{-}OC\text{-}HN\text{-}R\text{-}NH\text{-}CO\text{-}OR^1 \qquad (V)$$

in a reaction mixture which also contains the alcohol $R^1\text{-}OH$ and high-boiling residues and may further contain a dialkyl carbonate $R^1\text{-}O\text{-}CO\text{-}O\text{-}R^1$ and/or an alkyl carbamate $R^1\text{-}O\text{-}CO\text{-}NH_2$;

c) removing the alcohol, the dialkyl carbonate and/or alkyl carbamate from the resulting reaction mixture, and recycling the alcohol into the reaction stage a), to obtain the reaction mixture containing the cycloalkylenediurethane of the formula (V) and the high-boiling residues;

d) optionally removing the high-boiling residues from the resulting reaction mixture;

e) thermally cleaving the reaction mixture containing the cycloalkylenediurethane purified by the stage c) and alone or in combination with the stage d) without solvent in the presence of a catalyst, at a temperature of from 180 to 280°C and under a pressure of from 0.1 to 200 mbar, in such a way that from 10 to 60% by weight of the reaction mixture is constantly discharged from a bottom, to obtain a cleavage product;

f) separating the cleavage product by rectification into the cycloaliphatic diisocyanate of the formula (I) in a crude form and the alcohol of the formula (III);

g) purifying the crude cycloaliphatic diisocyanate by distillation, and isolating a pure product fraction of the cycloaliphatic diisocyanate;

h) reurethanizing a bottoms discharge from the stage e) by a partial or full reaction with the alcohol separated from the stage f), in the presence or absence of a catalyst for from 1 to 150 min, at a temperature of from 20 to 200°C and at a pressure of from 0.5 to 20 bar;

i) separating a reurethanized stream from the stage h) into a material-of-value stream rich in a reurethanized product and a waste stream and discarding the waste stream rich in the high boiler residues;

j) conducting a portion of a bottom fraction of the purification by distillation stage g) into the cleavage reaction stage e) or into the urethanization stage h);

k) optionally, recycling a top fraction obtained in the purification by distillation stage g) into the reurethanization stage h); and

l) recycling the material-of-value stream from the separation stage i) into at least one of the stages b), c) and e).

3. The process of claim 2, wherein the cycloaliphatic diamine is 4,4′-dicyclohexylmethanediamine, 2,4-dicyclohexylmethanediamine, 2,2′-dicyclohexylmethanediamine, or a mixture of at least two of these isomers.

4. The multistage process of claim 2, wherein the cycloaliphatic diamine is 4,4′-dicyclohexylmethanediamine or an isomeric mixture of dicyclohexylmethanediamines (H_{12}MDA).

5. The multistage process of claim 2, wherein the cycloaliphatic diamine is 1,4-diaminocyclohexane.

6. The process of any one of claims 2 to 5, wherein the reaction of the stage a) is carried out in a distillation reactor.

7. The process of any one of claims 2 to 6, wherein the reaction of the stage a) is effected in a molar ratio of the diamine : urea : the alcohol of from 1:2.0:3 to 1:2.4:10.

8. The multistage process of any one of claims 2 to 7, wherein, in the stage a), the diamine and urea are supplied continuously to an uppermost tray and ammonia

released is driven out by vapor of the alcohol which is introduced into a bottom of a distillation reactor.

9. The process of any one of claims 2 to 8, wherein the diamine and urea stay for a residence time in the stage a) of from 4 to 10 hours.

10. The process of any one of claims 2 to 9, wherein the stage b) is carried out in a pressure distillation reactor.

11. The process of any one of claims 2 to 10, wherein the stage b) is conducted at a molar ratio of the bisurea to the alcohol of 1:5 to 12.

12. The process of any one of claims 2 to 11, wherein the cycloalkylenebisurea from the stage a) is conducted to an uppermost tray of the second reactor of the stage b).

13. The process of any one of claims 2 to 12, wherein the reaction in the stage b) is carried out at a reaction temperature of from 160 to 250°C and under a pressure of from 7 to 15 bar.

14. The process of any one of claims 2 to 13, wherein the reaction in the stage b) takes place within 2 to 20 hours.

15. The process of any one of claims 2 to 14, wherein the reaction in the stage b) is carried out in the presence of a catalyst.

16. The process of any one of claims 2 to 15, wherein the alcohol of the formula (III) has 1 to 6 carbon atoms.

17. The process of any one of claims 2 to 16, wherein the alcohol of the formula (III) is 1-butanol.

18. The process of any one of claims 2 to 17, wherein the stage c) is carried out in two stages; in a first stage, the reaction mixture is decompressed from a pressure level of the reaction stage b) to a pressure of 1 to 500 mbar, to form a liquid effluent and a gaseous vapor; and in a second step, any residual alcohol present, the dialkyl carbonate and the alkyl carbamate are removed from the liquid effluent by thin-film evaporation at a temperature of 180°C to 250°C and a pressure of 0.1 mbar to 20 mbar.

19. The process of claim 18, wherein the gaseous vapor containing the alcohol formed in the first stage is subjected to a further distillative purification and then is fed into the reaction stage a).

20. The process of any one of claims 2 to 19, wherein the removal stage d) is absent.

21. The process of any one of claims 2 to 19, wherein the removal stage d) is employed at a temperature of 180 to 260°C and under a pressure of 0.01 to 10 mbar, by using a thin-film or short-path evaporator; and the high-boiling residues so separated are discharged and discarded.

22. The process of claim 21, wherein the reaction mixture from the removal stage c), before it is transferred to the stage d), is divided into two substreams, of which one substream is fed directly to the cleavage stage e).

23. The process of any one of claims 2 to 22, wherein the thermal cleavage stage e) is carried out in a tubular furnace or an evaporator.

24. The process of any one of claims 2 to 22, wherein the thermal cleavage stage e) and the separation stage f)

are together carried out in a combined cleavage and rectification column.

25. The process of any one of claims 2 to 24, wherein the separation stage f) is effected at a temperature of 95 to 260°C and a pressure of 0.5 mbar to 250 mbar.

26. The process of any one of claims 2 to 25, wherein the purification stage g) is conducted by distillation at a temperature of from 95 to 260°C and under a pressure of from 0.5 mbar to 150 mbar.

27. The process of any one of claims 2 to 26, wherein the separation stage i) is effected by distillation at a temperature of from 180°C to 270°C and under a pressure of from 0.01 mbar to 10 mbar.

28. The process of any one of claims 2 to 26, wherein the separation stage i) is effected by extraction using supercritical carbon dioxide as an extractant.

29. The process of any one of claims 2 to 28, wherein the reurethanized stream before the separation stage i) is divided into two substreams in a ratio of from 99:1 to 1:99, of which one is fed directly to the purification stage c) and the other to the separation stage i).

30. The process of any one of claims 2 to 29, wherein the separation stage i) is carried out in a continuous tank battery or in a tubular reactor.

31. The process of any one of claims 2 to 30, wherein the reurethanization reaction stage h) is effected in the presence of a catalyst selected from the group consisting of carboxylates or halides of tin, zinc or copper, tertiary amines and iron halides.

32. The process of claim 1, wherein the diamine is selected from the group consisting of 1,3- or 1,4-diaminomethylcyclohexane, hexane-1,6-diamine, 2,2,4- or 2,4,4-trimethylhexan-1,6-amine and 3-aminomethyl-3,5,5-trimethylcyclohexylamine.

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