



(22) Date de dépôt/Filing Date: 1993/05/14

(41) Mise à la disp. pub./Open to Public Insp.: 1993/11/16

(45) Date de délivrance/Issue Date: 2006/02/21

(30) Priorité/Priority: 1992/05/15 (MI92 A 001170) IT

(51) Cl.Int./Int.Cl. *C07C 263/00* (2006.01),
C07C 265/00 (2006.01)

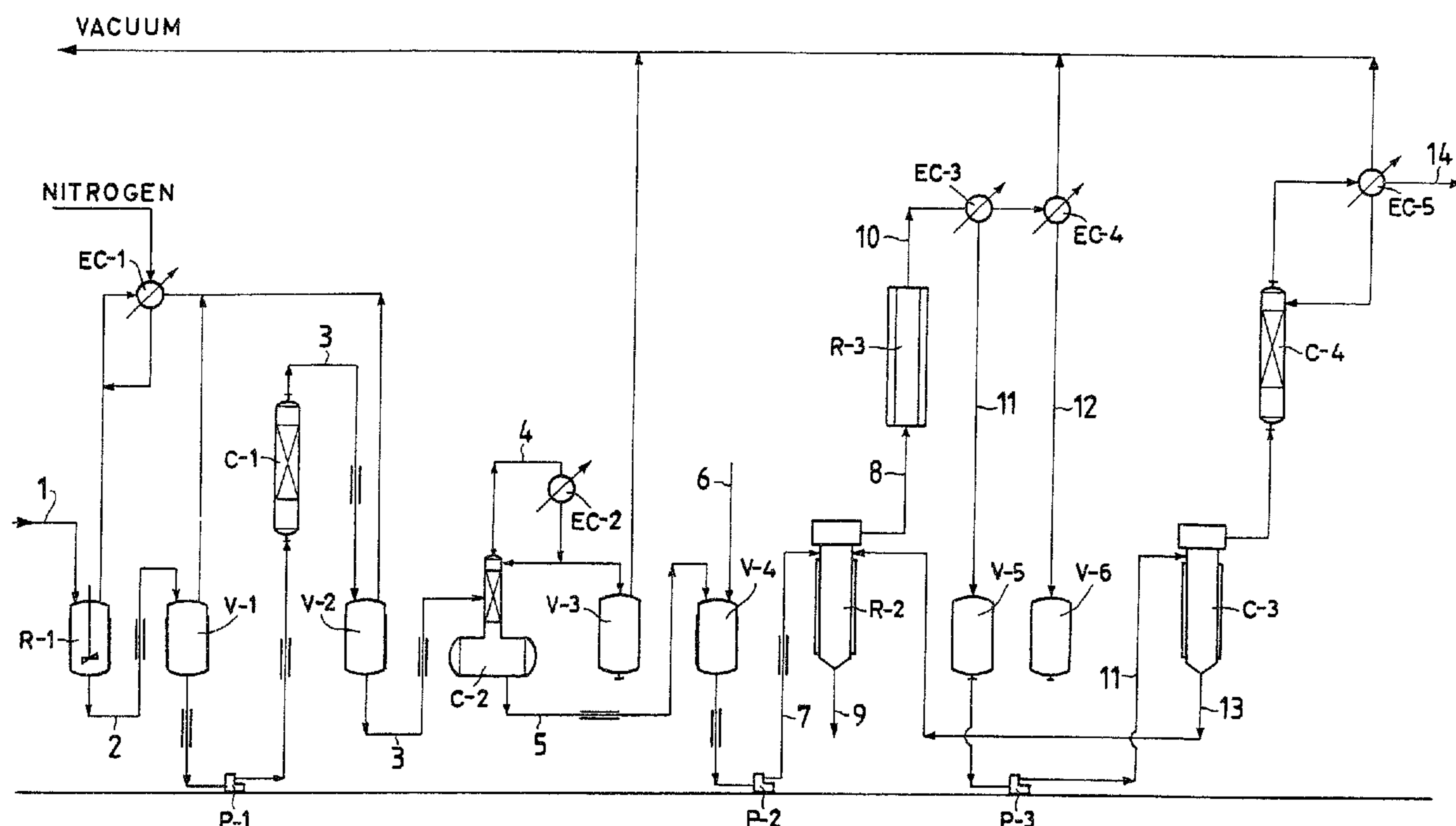
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(54) Titre : METHODE DE PREPARATION D'ISOCYANATES D'ALKYLE

(54) Title: PROCESS FOR THE PREPARATION OF ALKYL ISOCYANATES



(57) Abrégé/Abstract:

Multistep process for the preparation of alkyl mono and diisocyanates consisting in reacting the corresponding aliphatic amine or diamine with dimethylcarbonate and, substantially, in partially vaporizing and converting the urethane thus formed in an evaporator to subsequently terminate the cracking in a II° reactor, and finally subjecting the cracking product to fractional distillation at reduced pressure, recycling the unconverted part to the partial vaporization step.

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PROCEDURE FOR THE PREPARATION OF ALKYL ISOCYANATES.

Abstract

Multistep process for the preparation of alkyl mono and diisocyanates consisting in reacting the corresponding
5 aliphatic amine or diamine with dimethylcarbonate and, substantially, in partially vaporizing and converting the urethane thus formed in an evaporator to subsequently terminate the cracking in a II° reactor, and finally subjecting the cracking product to fractional
10 distillation at reduced pressure, recycling the unconverted part to the partial vaporization step.

PROCESS FOR THE PREPARATION OF ALKYL ISOCYANATES.

The present invention relates to a process for the preparation of alkyl mono and diisocyanates consisting in the conversion of an alkyl mono or diamine
5 into the corresponding urethane by reaction with dialkyl carbonate and the subsequent thermal decomposition of the urethane groups into isocyanate. This process has the great advantage of not using toxic compounds as raw materials.

10 Various processes for the preparation of isocyanates starting from aminic compounds via dialkylcarbonate are already described in literature: for example, patent applications

WO 8805430; JP 2066-261; JP 2311-452

15 disclose a two-step process consisting in:

- 1) reacting a diamine with dimethylcarbonate in the presence of an alkaline alcoholate to produce urethane which is recovered from the mixture;
- 2) the decomposition of the latter at 230°C in an
20 organic solvent having a high boiling point in the presence of a metal and continuously removing the

reaction products, by distillation.

Between 1) and 2) the catalyst is neutralized by treatment with acid, and then removed; the urethane is then purified by distillation.

5 This process has a problem in step 1) concerning the recovery of the dialkylurethane by distillation with the conventional methods, which is difficult to perform with good yields, and in step 2) various problems due to the purification of the liquid flows
10 from the catalytic residues.

US patents 4.596.678 and 4.596.679 also describe a two-step process consisting in:

- 1) reacting a diamine with urea in the presence of dialkylcarbonate and alcohol to give the corresponding alkyl diurethane;
15
- 2) subjecting the latter to partial vaporization and be then fed to a cracking reactor packed with a metallic filling with a low pressure loss which operates at a temperature which is higher than
20 300°C.

Between 1) and 2) the urethane, which however contains synthetic by-products, which have a negative influence on the final result, is isolated.

US patent 4.613.466 discloses a one-step process
25 wherein dialkylurethane urethane is partially vaporized without decomposition and fed as such to a cracking reactor packed with a specific metallic filling having

a catalytic function.

The products are then recovered by fractional condensation.

The above two-step process has, as already mentioned, the serious disadvantage of insufficient selectivity in the synthesis of the urethane during which are formed complex mixtures which are difficult to separate; the second step of the process and also the procedure described in the last patent have problems deriving from the presence of polymeric by-products in the alkyl diurethane, which must be removed from the vaporization chamber by the liquid current discharged (partial evaporation) and from which it is difficult to recover the alkyl diurethane. This weighs heavily on the specific consumption of the process.

The present invention consequently relates to a process for the preparation of alkyl mono and diisocyanates which overcomes all the disadvantages arising in the processes of the known art, and does not necessitate, as already stated, raw materials which are classified as toxic.

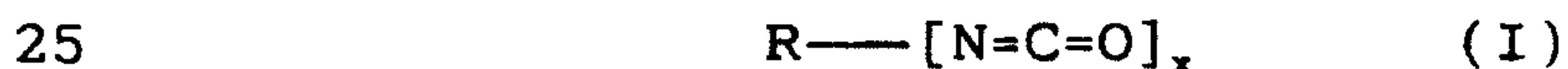
This process basically consists in the conversion of an alkyl mono or diamine into the corresponding urethane and the subsequent thermal decomposition of the urethane groups.

In particular it has been found that it is possible to obtain alkyl mono and diurethanes having a high

purity with quantitative yields of the alkyl mono and diamine used, using dimethylcarbonate as a carbonylation agent in the presence of a basic catalysts selected from the alcoholates of alkaline and alkaline earth metals. These alkyl diurethanes are then fed to a cracking chamber where they undergo thermal treatment under such conditions of pressure and temperature as to allow complete vaporization and partial conversion in the useful cracking product. The mixture of vapours discharged is then fed to a subsequent cracking reactor which operates at a higher temperature and, however sufficient to make the conversion substantially complete. This stream of vapours is then subjected to fractional condensation to separate its constituents. The useful product is then recovered from the condensate stream, by distillation.

It has been found that operating with this kind of process it is possible to obtain alkyl mono and diisocyanates from the corresponding aminic compounds with high yields.

In accordance with the above and according to a more precise definition, the present invention relates to a process for the production of isocyanates having the formula:



wherein x represents an integer selected from 1 or 2, and R represents an alkyl radical with a number of

carbon atoms of up to 10, either linear or branched, unsubstituted or having substituents selected from alkoxy groups, halogen or cycloalkyl radicals; or a cycloalkyl radical with a number of carbon atoms of between 5 and 7, again either unsubstituted or having substituents selected from those specified above, a procedure which includes the following steps:

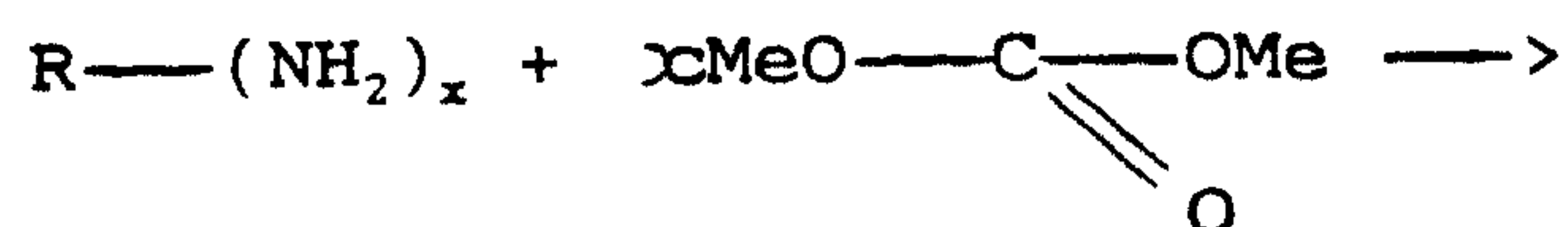
a) reaction of an amine having the formula



with dimethylcarbonate in the presence of a basic catalyst selected from the alcoholates of alkaline or alkaline-earth metals to give methylurethanes having the formula



according to the reaction



with x and R which have the above-defined meanings;

- b) neutralization of the basic catalyst;
- c) removal of the alcohol and any excess of dimethylcarbonate;
- d) vaporization with partial cracking of the methylurethane obtained in step a);
- e) exhaustive cracking of the urethane;
- f) fractional distillation at reduced pressure of the

cracking products with possible recycling of to the unconverted part in step d).

Isocyanates which can be advantageously obtained according to the procedure of the present invention are
5 butylisocyanate, cyclohexylisocyanate, hexamethylenediisocyanate and isophoronediiisocyanate.

The process of the present invention may be described in further detail as follows:

- in a first step the dimethyl carbonate is reacted
10 with the amine in continuous or batch in a molar ratio of between 1/1 and 10/1 and in the presence of the catalyst in quantities of between 0.01 and 0.15 moles per amino equivalent to be reacted. Particularly suitable catalysts are the sodium
15 alcoholates derived from C_1 ÷ C_4 linear or branched alcohols: above all, sodium methoxide.

The reaction is carried out within a temperature of 40 to 90°C for a period of time ranging from 0.2 to 4 hours.

- 20 In accordance with this there is a complete or substantially complete conversion of the amino groups to form a mixture of urethane and methanol according to the above reaction.

The catalyst is neutralized, preferably maintaining the reaction temperature, by treatment with an
25 organic or inorganic acid, in the homogeneous or heterogeneous phase, of the reacted mixture.

Acids which can be used for the purpose are preferably the mono and di-carboxylic acids, the alkyl or aryl sulphonic acids also in the form of ion-exchange resins and the phosphoric acid.

5 The urethane is recovered by removing the alcohol and possible excess of carbonate by distillation with a pressure ranging from 200 to 760 mm Hg and boiler temperature of between 40 and 140°C;

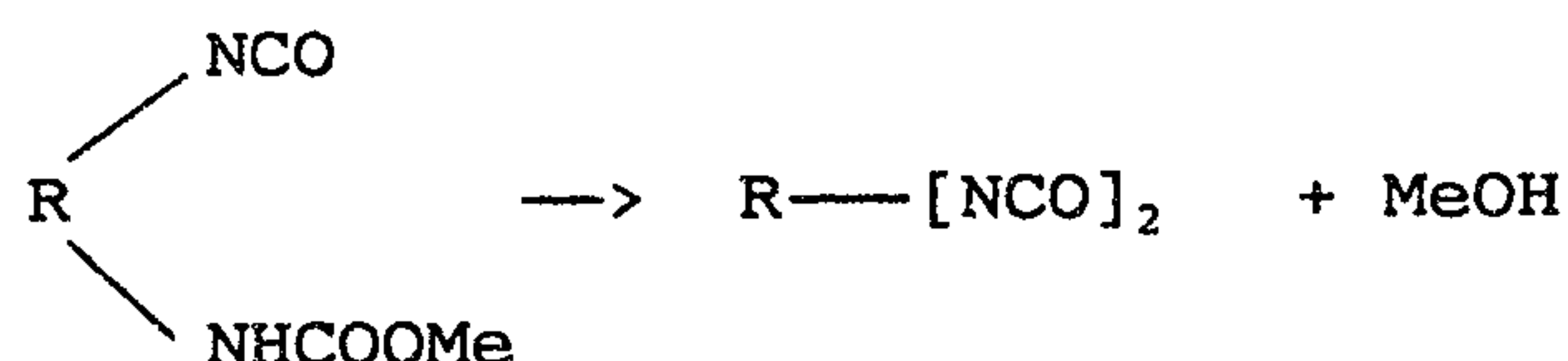
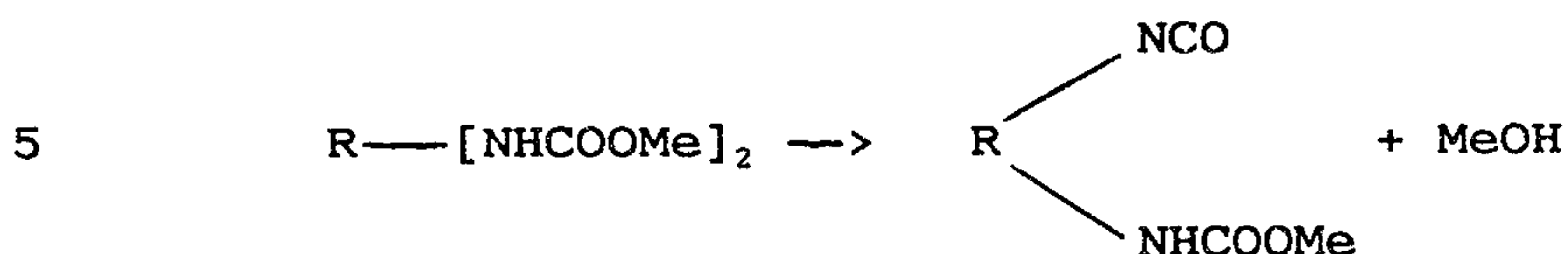
- in a second reaction step the liquid urethane
10 either pure or in solution with a high-boiling solvent in a weight ratio of the latter with respect to the urethane of between 1/1 and 0.1/1, is fed into a cracking chamber. In a preferred embodiment a recycled current is also fed from the
15 third step as described later.

This cracking chamber is fed with a LHSV space velocity of between 1 and 6 hr^{-1} , and operates within a temperature range of 150 to 300°C and a pressure of between 0.5 and 760 mmHg.

20 The mixture of vapours obtained is continuously fed to a second cracking chamber with a GHSV space velocity rate of between 10 and 100 hr^{-1} , maintaining it conveniently in equipressure with the previous chamber and with a temperature range of
25 300 to 600°C.

In accordance with this there is a complete conversion of the urethane to isocyanate mixed

with alcohol and also possibly with an intermediate which can be formed when x is 2, according to the following equations:



10 This mixture of vapours is then subjected to fractional condensation obtaining within a temperature range of 50 to 120°C, a liquid fraction basically containing the final product possibly mixed with the above intermediate. If desired a
15 second liquid fraction can be obtained within a temperature range of -40 to +20°C basically containing methanol.

- in a third step of the procedure the flow of condensate containing an abundance of the useful
20 product is fed continuously or semi-continuously to a distillation apparatus composed of a boiler equipped with a column. This apparatus generally operates with a brief contact time and at a reduced pressure which causes the condensation of
25 isocyanate vapours (I) in a temperature range of between 10 and 150°C.

In accordance with this a stream of condensed

vapours is obtained from the head of the column, in a typical weight ratio with the feeding of between 0.5/1 and 0.8/1, mainly composed of the useful product with a purity which is higher than 99.5% parts by weight. From the bottom of the column a residue liquid flow is obtained composed of isocyanate possibly mixed with the intermediate which is formed when x corresponds to two. This stream, as already specified, in a preferred embodiment is recycled as a liquid to the first cracking chamber (second step).

The embodiment herein described affords a useful product with particularly high yields because the vaporization under cracking conditions starting from high purity urethanes produces isocyanates with an unexpected improved selectivity with respect to the procedures of the known art. In addition, the embodiment herein described enables the isocyanates to be recovered and purified without the use of diluents and without the formation of polymeric by-products owing to the combination of benefits deriving from distillation at reduced pressure and those deriving from a reduction of the contact times.

The experimental examples which follow provide a further illustration of the present invention, but naturally do not limit it in any way.

EXAMPLE 1

In the present example is adopted the equipment outlined in fig. 1.

The first step of the procedure is carried out in the equipment composed of:

R1, C1, C2, V1, V2, V3, EC-1, EC-2 and P1.

The condensers EC-1 and EC-2 are brought to an operating temperature of about 15-20°C.

102.8 parts by weight of anhydrous (50 ppm max of water) dimethylcarbonate (hereinafter referred to as DMC) and 0.3 parts of sodium methoxide (hereinafter referred to as CH_3ONa) in a 30% p. solution of methanol are charged into the reactor R1 at atmospheric pressure.

15 R1 is heated to 65°C, then 33.1 parts of liquid hexamethyldiamine (hereinafter referred to as HDA) kept under nitrogen are fed in portions. At the end of the reaction a flow (2) is fed to V1 (conditioned at 65°C), consisting of 136.0 parts composed of:

20 48.7% bw of bis-N (1.6) hexamethylene O-methyl urethane (hereinafter referred to as HDU)

37% bw of DMC

14.1% bw of methanol and

0.22 bw of CH_3ONa

25 The neutralization of CH_3ONa is carried out in the dehydrated and conditioned column C1 which contains a bed of resin with sulphonic ion-exchange of which the

concentration of acidic hydrogen ions is known such as for example Amberlyst-15 (spherical particles) (supplied by ROHM and HAAS).

The flow (2) is volumetrically fed from V1 to C1, 5 conditioned at 65°C, with a volumetric rate equal to 1 volume of bed per hour. A liquid flow (3) is obtained from C1 in a weight ratio with (2) equal to 0.99/1 containing:

49% p HDU, 37% p DMC, 14% p methanol with a residue 10 content of sodium lower than 0.3 ppm. This flow (3) is collected in V2 suitably thermostat-regulated at 65°C.

The HDU is isolated in the batch column C2 for the vaporization of DMC and methanol. The above-mentioned flow (3) is fed from V2 to C2, initially at 65°C, the 15 temperature of the bottom is then gradually brought, at atmospheric pressure, to a maximum of 140°C and these conditions are left until the vapours have been exhausted eventually completing by decreasing the pressure to 400 mmHg.

20 68.7 parts of a stream of vapours (4) are obtained from C2, which is condensed in EC-2 and collected in V3, composed of:

72.5% p of DMC, 27.5% p of methanol.

66.0 parts of a bottom liquid stream (5) of HDU 25 having a purity higher than 99.5% parts by weight with a content of residuous sodium lower than 0.5 ppm are also obtained from C2 and collected in V4.

From the above data a yield of HDU based on HDA equal to 99.7% can be calculated for the first step.

The second step of the procedure is carried out in equipment composed of:

5 R2, R3, C3, C4, EC-3, EC-4, V4, V5, V6 and P2.

The reactor R2 is composed of a thin film evaporator, reactor R3 is tubular with a length of 1500 mm and internal diameter of 24.8 mm. This reactor is made of AISI 316L steel and is packed with a low pressure loss
10 packing of the same material in the form of flakes.

EC-3 is brought to +60°C and EC-4 to -20°C, the system of reactors R2 and R3 is brought to a value of residual pressure equal to 75 mmHg measured at the outlet of R2; R2 is heated to 290°C and R3 to 420°C.
15 Under these conditions 66 parts of a flow (7) composed of liquid HDU having a purity greater than 99.5% with and a content of sodium residue lower than 0.5 ppm, are fed from V4 to R2 with an LHSV space velocity of 1.4 hr⁻¹. 64 parts of a gaseous flow (8) are removed from
20 R2, containing:

3.34% bw of methanol;

1.36% bw of hexamethylendiisocyanate (hereinafter
HDI);

17.6% bw of hexamethylene monourethane monoisocyanate
25 (hereinafter HMI);

77.34% bw of HDU.

2.32 parts of a liquid stream (9) having the

following composition are also taken from R2:

57.7% bw HDU and

42.2% bw of polymeric by-products (polyureas).

As already mentioned 64 parts of the stream of
5 vapours (8) already described are fed from R2 to R3
with a GHSV space velocity equal to 38 hr^{-1} . 64 parts of
a stream of vapours (10) containing the following are
taken from R3:

67.23% bw HDI;

10 5.98% bw HMI and

26.6% bw of methanol

which is partially condensed in EC-3. 46.5 parts of a
liquid stream (11) containing the following are
obtained from EC-3:

15 91.6% bw HDI and

8.17% bw HMI

which is collected in V5. 16.8 parts of a gaseous
stream (12) containing mainly methanol are also
obtained from EC-3 which is subsequently condensed in
20 EC-4 and collected in V6.

From the above data a conversion of HDU of 97.9%,
a selectivity to HDI of 91.0% and a selectivity to HMI
of 6.8% are calculated for the second step.

The third step of the procedure is carried out in
25 equipment composed of C3, C4, EC-5 and P3.

Column C3 is composed of a falling-film evapora-
tor, column C4 is a distillation column of the conven-

tional packed type.

The condenser EC-5 is brought to 20°C. Columns C3 and C4 are brought to a residual pressure value of 5 mmHg measured at the head of C4, C3 is heated to 131°C.

5 Under these conditions 46.5 parts of the liquid flow (11) already described are fed from V5 to C3 with a flow rate related to the exchange surface of $3 \text{ kg} \times \text{hr}^{-1} \times \text{m}^{-2}$.

32.9 parts of a stream of vapours (14), taken from
10 C4 and condensed in EC-5, are composed of the product HDI with a purity higher than 99.5% by weight. 13.6 parts of a liquid flow (13) having the following composition are taken from C3:

71.1% bw HDI,

15 27.8% bw HMI

which as already specified in the preferred embodiment is subsequently fed to reactor R2 of the second step.

From the above data a mass balance of HDI equal to 100% and a molar balance of HMI equal to 100% are
20 calculated for the third step. The recovery yield of HDI is equal to 77% per passage.

CLAIMS

1. A process for the preparation of an alkyl mono and diisocyanate having the formula:



wherein x represents an integer equal to 1 or 2, and R represents an alkyl radical with a number of carbon atoms of up to ten, either linear or branched, unsubstituted or
10 having substituents selected from alkoxy groups, halogens or cycloalkyl radicals; or a cycloalkyl radical with a number of carbon atoms of between 5 and 7, again either unsubstituted or having substituents selected from those specified above, which comprises the following steps:

a) reaction of an amine having the formula:



wherein x and R are defined as above, with dimethyl
20 carbonate in the presence of a basic catalyst;

b) neutralization of the reaction mixture obtained in step a), which mixture contains an urethane, by treatment with an organic or inorganic acid, in the homogeneous or heterogeneous phase;

c) removal, from said mixture, of the alcohol formed and any excess of dimethyl carbonate;

d) feeding the reaction mixture, treated according to steps (b) and (c) to a first reactor in which the urethane is completely vaporized and partially converted into
30 cracking products;

e) feeding the stream of vapours obtained from step (d) to a second reactor in which exhaustive cracking of the urethane is carried out;

f) fractional distillation at reduced pressure of the cracking product with optional recycling of the unconverted part to step (d).

10 2. The process according to claim 1, wherein the reaction in step a) takes place in the presence of a catalyst selected from the alcoholates of alkaline or alkaline-earth metals.

3. The process according to claim 2, wherein the reaction takes place in the presence of sodium methoxide.

4. The process according to claim 2, wherein the reaction takes place in the presence of a quantity of catalyst of between 0.01 and 0.15 moles per amino equivalent.

5. The process according to claim 1, wherein the reaction of step a) is carried out at a temperature ranging from 40 to 90°C.

20 6. The process according to claim 1, wherein the reaction of step a) is carried out with a molar ratio between the dimethyl carbonate and the amine of between 1/1 and 10/1.

7. The process according to claim 1, wherein the vaporization with partial cracking in step d) is carried out at a temperature ranging from 150 to 300°C.

8. The process according to claim 1, wherein the vaporization with partial cracking of step d) is carried out

within a pressure range of 0,067 and 101,3 kPa (0.5 to 760 mmHg) .

9. The process according to claim 1, wherein the vaporization with partial cracking of step d) is carried out in a thin-film evaporator.

10. The process according to claim 1, wherein the exhaustive cracking in step e) is carried out at a temperature ranging from 300 to 600°C.

10 11. The process according to claim 1, wherein the exhaustive cracking of step e) is carried out in a tubular reactor.

12. The process according to claim 1, wherein the fractional distillation in step f) is carried out at a temperature ranging from 10 to 150°C.

13. The process according to claim 1, wherein the fractional distillation of step f) is carried out in a thin-film evaporator whose vapours are fed into a distillation column.

20 14. The process according to claim 9, wherein the vaporization with partial cracking of step d) is carried out by feeding the urethane obtained in step c) in solution of a high-boiling solvent to the evaporator in a weight ratio of solvent to urethane of between 1/1 and 0.1/1.

Fig.1

