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(54) **UN PROCÉDE DE PURIFICATION D'ISOCYANATES**

**ORGANIQUES, LES ISOCYANATES ORGANIQUES AINSI  
PURIFIÉS ET LEUR UTILISATION**

(54) **A PROCESS FOR PURIFYING ORGANIC ISOCYANATES, THE  
ORGANIC ISOCYANATES SO PURIFIED AND THEIR USE**

(57) The invention provides a new process for purifying organic isocyanates or isocyanate mixtures by mixing the isocyanates or isocyanate mixtures to be purified with at least one alcohol and/or thiol or a mixture of alcohols and/or thiols, heating the resultant mixture and simultaneously or subsequently degassing the mixture and/or working up the mixture by distillation and/or extraction.



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LeA 33,370

A PROCESS FOR PURIFYING ORGANIC ISOCYANATES, THE  
ORGANIC ISOCYANATES SO PURIFIED AND THEIR USE

ABSTRACT OF THE DISCLOSURE

The invention provides a new process for purifying organic isocyanates or isocyanate mixtures by mixing the isocyanates or isocyanate mixtures to be purified with at least one alcohol and/or thiol or a mixture of alcohols and/or thiols, heating the resultant mixture and simultaneously or subsequently degassing the mixture and/or working up the mixture by distillation and/or extraction.

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5            A PROCESS FOR PURIFYING ORGANIC ISOCYANATES,  
              THE ORGANIC ISOCYANATES SO PURIFIED AND THEIR USE

BACKGROUND OF THE INVENTION

                                 The present invention provides a new process for purifying one or  
                                 more organic isocyanates or isocyanate mixtures. In this process, the  
10            isocyanate material to be purified is combined with one or more alcohols  
                                 and/or thiols or mixtures of alcohols and/or thiols, the resultant mixture is  
                                 heated and, optionally, simultaneously with or subsequent to being heated,  
                                 degassed and/or worked up by distillation and/or extraction.

                                 Impurities of varying types and amounts are generally present in  
15            organic isocyanates due to the method used for their preparation. These  
                                 impurities are the cause of variable activity. Variable activity adversely  
                                 affects the reproducibility of product properties and thus the economic  
                                 viability of using the isocyanate having variable activity. Both aromatic  
                                 isocyanates (for example the well-known phosgenation products of aniline/  
20            formaldehyde condensation and 2,4- and 2,6-diisocyanatotoluene) and  
                                 aliphatic isocyanates (such as isophorone diisocyanate) contain a whole  
                                 range of impurities of this type. These impurities are mainly chlorine-  
                                 containing compounds which cause variations in the activity if the chlorine  
                                 is "highly mobile" (i.e., so-called "hydrolyzable") chlorine. Some of these  
25            compounds have been shown to be relatively stable and they remain in  
                                 the isocyanate even after distillation. They also exert a harmful effect on  
                                 the stability of an isocyanate as well as on its activity. A more uniform,  
                                 smaller proportion of these contaminants, resulting in activity  
                                 standardization and simpler subsequent processing of isocyanates is  
30            therefore of both technical and economic importance.

                                 There have been many attempts to find opportunities for removing  
                                 the chlorine-containing compounds from isocyanates. Additives based on

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metals or alkali metals such as metal oxides, metal cyanamides, metal hydrides, metal fatty acid esters in the presence of sterically hindered phenols, metal naphthenates, metal silicates, alkali metal carbonates and organometallic compounds are described in JP 4 501 032 9 B;

5 JP 4 200 413 7 B; JP 5 908 845 2 A; JP 5 910 875 3 A; JP 5 917 245 0 A; US-A 3,373,182; GB-A 1 111 581; US-A 3,759,971; US-A 4,094,894; ZA 8 100 606; DE-A 11 38 040; DE-A 12 86 025; US-A 3,458,558; US-A 3,264,336; SU 8 066 77 and DE-A 22 10 607. In each of the processes disclosed in the patents and published applications mentioned

10 above, a number of engineering difficulties which relate to isolation of the metal-containing additives or the restricted use of metal-containing isocyanates and/or distillation residues are encountered.

Similar difficulties are encountered when using additives such as the imidazole described in GB-A 1 347 647 and JP 0 505 898 2 A; the

15 sulfonic acids and their esters described in GB-A 1 458 747; the diethyl sulfate described in GB 1 459 691 and the sulfuric acid also described there; the trialkyl phosphate described in DD 288 596; and the use of other additives such as epoxy compounds (DE-A 22 49 375; JP 0 932 396 8 A2), tetra-substituted ureas (DD 288 598), formic or acetic acid or their

20 derivatives (US-A 3,799,963) or the compounds which contain trimethylsilyl groups described in EP-A 524 507.

Some compounds with at least one Zerewitinoff-active NH group, such as urea (DD 285 594), biurets (DD 288 597), caprolactam (DD 285 593), ammonium salts (DD 288 594), carbodiimides (DD 288 599), primary

25 and secondary amine salts (DD 288 593), tertiary alcohols and tertiary alkyl carbamates (DD 288 595) are recommended in the prior art for purifying isocyanates. Here again, isolation of the additives or the restricted use of additive-containing isocyanates and/or distillation residues, and in particular the sometimes large decrease in NCO index

30 and the increase in viscosity, which can be attributed to the production of biurets when using tertiary alcohols, are disadvantages. The latter also

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applies to the use of water for purifying isocyanates (DE-A 12 40 849).

From publications JP 6 116 125 0 A; JP 0 516 323 1 A;  
DE-A 19 50 101; DE-A 19 38 384; DE-A 25 32 722; DE-A 26 31 168;  
US-A 3,853,936; FR-A 1 555 517; DE-A 29 33 601; and US-A 3,549,504, it  
5 is known that isocyanates can be purified by specific distillation and  
crystallization techniques.

It is also known that heating isocyanates, particularly when  
simultaneously stripping with an inert gas, or heating in an inert solvent  
under pressure with simultaneous removal by suction of the volatile  
10 compounds, reduces the concentration of readily decomposable chlorine  
compounds. (See, e.g., DE-A 12 70 036; DD 271 820; US-A 3 219 678;  
GB-A 1 080 717; DE-A 22 37 552; US-A 3,857,871; US-A 1,458,223;  
JP 0 727 808 8 A2; JP 0 634 570 7 A2; and GB 1 384 065.) It is mainly  
the concentration of readily decomposable chlorine compounds that can  
15 be determined analytically as acidity which is decreased, whereas short-  
term heating may suppress the formation of sediments (US-A 3,274,225).

#### SUMMARY OF THE INVENTION

It is an object of the present invention to provide a new process for  
purifying organic isocyanates which effectively removes impurities without  
20 creating the engineering difficulties experienced with prior art processes.

This and other objects which will be apparent to those skilled in the  
art are achieved by combining the isocyanate to be purified with an  
additive corresponding to a specified formula, heating the additive-  
containing isocyanate for at least 5 minutes at a temperature of from about  
25 100 to about 250°C, and at the same time or subsequently the isocyanate  
being treated is stripped with an inert gas and/or is worked up by  
distillation and/or extraction.

#### DETAILED DESCRIPTION OF THE PRESENT INVENTION

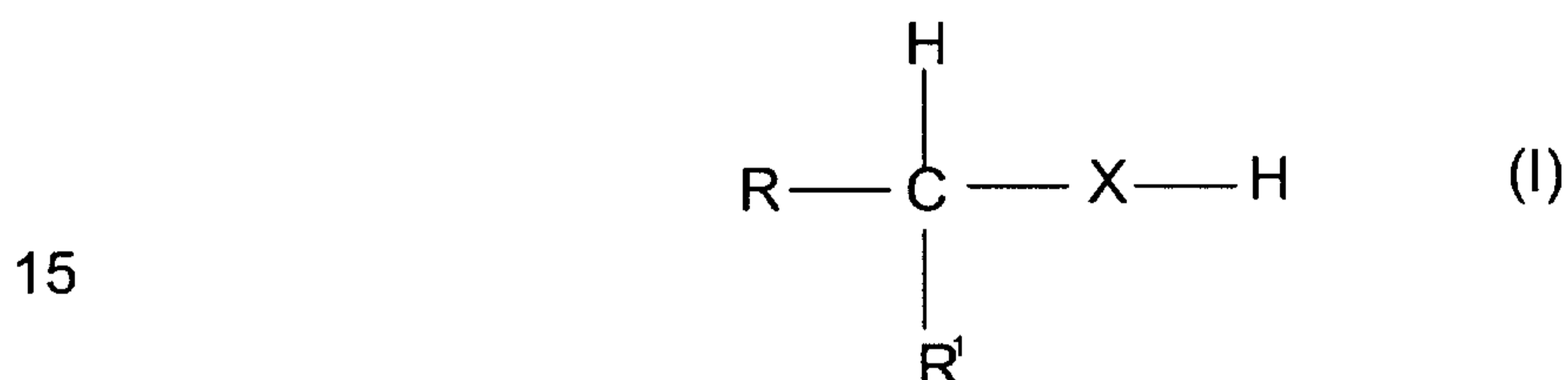
The present invention relates to a process in which a small amount  
30 of at least one compound corresponding to Formula (I) described in more  
detail below is added to the organic isocyanate being treated, the

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isocyanate containing the compound corresponding to Formula (I) is then heated for a certain time, if required under elevated or reduced pressure, and at the same time or subsequently the isocyanate being treated is stripped with an inert gas and/or is purified by a single distillation and/or  
5 extraction procedure.

In the process for purifying organic isocyanates or isocyanate mixtures of the present invention, the organic isocyanate(s) or isocyanate mixture(s) is heated with a total of from about 0.01 to about 10 wt.%, based on the weight of organic isocyanate or isocyanate mixture, of at  
10 least one compound having a structure corresponding to Formula (I) or mixtures of compounds corresponding to Formula (I) below:



in which

X represents O or S and

R and R<sup>1</sup>, independently represent H, or a C<sub>1</sub>-C<sub>36</sub>-alkyl, C<sub>6</sub>-C<sub>36</sub>-aryl, C<sub>3</sub>-  
20 C<sub>36</sub>-cycloalkyl or C<sub>7</sub>-C<sub>36</sub>-aralkyl group, or the groups R and R<sup>1</sup> may be linked via a ring system, or a primary X—H group, or a secondary X—H group,

R and R<sup>1</sup> may also contain any of the previously specified groups which may further contain functional groups that do  
25 not react with an isocyanate group

The isocyanate containing the compound corresponding to Formula (I) is heated for at least 5 min. at 100 to 250°C, with or without a solvent that is not reactive towards isocyanate groups, under elevated or reduced pressure, if necessary, and at the same time or subsequently is stripped  
30 with an inert gas and/or is worked up by distillation and/or extraction.

The organic isocyanates which may be purified by the process of

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the present invention are suitable as starting compounds for preparing polyurethane plastics by the isocyanate/polyaddition process, in particular when preparing polyisocyanates which are used as hardeners for surface coatings.

5           The starting materials for the process of the present invention include any organic isocyanate. Examples of suitable isocyanates include:

- a)       mono-isocyanates with aliphatically, cycloaliphatically, araliphatically or aromatically bonded isocyanate groups (e.g. butyl isocyanate, cyclohexyl isocyanate, phenyl isocyanate) or any  
10       mixture of such mono-isocyanates;
- b)       diisocyanates or higher-functional isocyanates with molecular weights in the range of from about 140 to about 400 with aliphatically, cycloaliphatically, araliphatically and/or aromatically bonded isocyanate groups such as 1,4-diisocyanatobutane, 1,6-  
15       diisocyanatohexane (HDI), 2-methyl-1,5-diisocyanatopentane, 1,5-diisocyanato-2,2-dimethyl-pentane, 2,2,4- or 2,4,4-trimethyl-1,6-diisocyanatohexane, 1,10-diisocyanatodecane, 1,3- and 1,4-  
diisocyanatocyclohexane, 1,3- and 1,4-bis-(isocyanatomethyl)-cyclohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatocyclohexane  
20       (isophorone diisocyanate, IPDI), 4,4'-diisocyanatodicyclohexylmethane, 1-isocyanato-1-methyl-4(3)-isocyanatomethylcyclohexane (IMCI), bis-(isocyanatomethyl)-norbornane, 2-methylpentane-2,4-  
diisocyanate, 1,3- and 1,4-bis-(2-isocyanatoprop-2-yl)-benzene (TMXDI), 2,4- and 2,6-diisocyanatotoluene (TDI), 2,4'- and 4,4'-  
25       diisocyanatodiphenylmethane, 1,5-diisocyanato-naphthalene, dipropylene glycol diisocyanate, 4-isocyanato-methyl-1,8-octane diisocyanate (nonane triisocyanate) and any mixture of such diisocyanates and/or higher functional isocyanates.

Diisocyanates and higher functional isocyanates are preferably  
30       used in the process of the present invention. Diisocyanates with aliphatically and cycloaliphatically bonded isocyanate groups are

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especially preferred.

The compounds corresponding to Formula (I) which may be used in the process of the present include monohydric or polyhydric, saturated or unsaturated, cyclic, linear or branched, primary and secondary alcohols, which preferably contain from 1 to 36, more preferably from 1 to 10, carbon atoms. Examples of suitable alcohols include: methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, n-pentanol, 2-hydroxypentane, 3-hydroxypentane, the isomeric primary and secondary methylbutyl alcohols, n-hexanol, n-heptanol, n-octanol, n-nonanol, 2-ethylhexanol, primary and secondary trimethylhexanols, cyclohexanol, benzyl alcohol, n-decanol, n-undecanol, n-dodecanol (lauryl alcohol), n-tetradecanol, n-pentadecanol, n-hexadecanol, n-heptadecanol, n-octadecanol (stearyl alcohol), 2,6,8-trimethylnonanol, 4-cyclohexyl-1-butanol, 2,4,6-trimethylbenzyl alcohol, branched and linear, primary and secondary alcohols and mixtures of these such as, for example, those sold by the Henkel Co. under the tradename Lorol, glycerol or other dihydric and higher-hydric alcohols with primary and/or secondary OH groups.

Compounds corresponding to Formula (I) which may be used in the process of the present invention also include monofunctional and polyfunctional, saturated or unsaturated, linear, branched or cyclic, primary and secondary thioalcohols which preferably contain from 1 to 36, most preferably about 10, carbon atoms and mixtures thereof.

The compounds with a structure corresponding to Formula (I) may, less preferably, contain other functional groups which are not reactive towards isocyanate groups such as esters, ethers or heteroatoms such as halogens (Cl, Br) or nitrogen in addition to the XH (X = O or S) group.

Obviously, in addition to mixtures of alcohols corresponding to Formula (I) and mixtures of thioalcohols corresponding to Formula (I), mixtures of alcohols and thioalcohols corresponding to Formula (I) may also be used in the process of the present invention. Solutions of compounds corresponding to Formula (I) or solutions of mixtures of

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compounds corresponding to Formula (I) in inert solvents (i.e., solvents which do not react with isocyanate groups) may also be used but use of such solutions is not preferred.

Aliphatic, primary C<sub>1</sub>-C<sub>10</sub>-monoalcohols or mixtures of aliphatic C<sub>1</sub>-  
5 C<sub>10</sub>-monoalcohols are preferably used in the process of the present invention. The use of n-butanol is particularly preferred.

The process of the present invention may also be carried out with phenols.

In the process of the present invention, the mixture of organic  
10 isocyanate and the compound corresponding to Formula (I), or of isocyanate mixture and a compound corresponding to Formula (I), or the isocyanate and a mixture of compounds corresponding to Formula (I) or the isocyanate mixture and a mixture of compounds corresponding to  
15 Formula (I), is heated with an amount of the compound or mixture of compounds corresponding to Formula (I) of from about 0.01 to about 10 wt.%, preferably from about 0.05 to about 5 wt.%, most preferably from about 0.1 to 2.5 wt.%, based on the weight of isocyanate or isocyanate mixture. The mixture being heated may optionally include an inert solvent (i.e., a solvent which is not reactive towards isocyanate groups). The  
20 isocyanate being treated is heated for a period of at least 5 min, preferably at least 240 min. to a temperature of from about 100 to about 250°, preferably at least 150°C, most preferably higher than 180°. If required, the mixture may be heated at an elevated or reduced pressure. The isocyanate being heated may be stripped with an inert gas during the  
25 heating process or afterwards and/or worked up by distillation and/or extraction. Working up by distillation is understood to mean, in the case of using distillable starting isocyanates, the preparation of pure compounds by distillation, for example in a thin layer evaporator or across a distillation bridge.

30 Obviously, instead of stripping with an inert gas, degassing under vacuum (for example 100 to 1 mbar) may equally preferably be performed.

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The percentages by weight mentioned for the compounds corresponding to Formula (I), or mixtures thereof, used in the process of the present invention may vary, depending on the equivalent weight of the compound(s) corresponding to Formula (I).

5           The NCO/XH ratio (where X = O, S) does not fall below 10 to 1 in the process of the present invention.

10           The organic isocyanate(s) treated in accordance with the invention exhibit reduced variation in activity. This can be readily demonstrated by the reduced values for hydrolyzable chlorine which translate into improved activities for foaming ability or improved color stability.

The invention is further illustrated but is not intended to be limited by the following examples in which all parts and percentages are by weight, unless otherwise specified.

#### EXAMPLES

15           The HC values cited refer to the concentration of hydrolyzable chlorine. All percentage data is given with respect to weight.

#### Examples

20           The amount of compound specified in Tables 1, 2 and 3 was added to 100 g of the organic isocyanate indicated and the mixture was stirred under a gentle stream of inert gas for the stated time at the stated temperature (= conditioning). After cooling, products of the process of the present invention were obtained. These products may optionally be distilled for further purification.

25           The product obtained in Example 7 according to the invention (Table 2) was distilled across a distillation bridge (head temperature 96°C; pressure:  $1.5 \times 10^{-2}$  mbar). 99.8 % purity (GC), pale-colored isophorone diisocyanate was obtained.

Table 1

	Example 1*	Example 2	Example 3	Example 4	Example 5	Example 6
Organic isocyanate	isophorone diisocyanate (IPDI)	isophorone diisocyanate (IPDI)	isophorone diisocyanate (IPDI)	hexa-methylene diisocyanate (HDI)	isophorone diisocyanate (IPDI)	isophorone diisocyanate (IPDI)
Alcohol used	-	methanol	decanol	1-butanol	stearyl alcohol	isobutanol
Wt.% of alcohol	-	0.4	2	1	3.6	1
Temperature	220°C	220°C	220°C	220°C	220°C	220°C
Reaction time [h]	6	6	6	6	6	6
HC value before conditioning	156 ppm	156 ppm	156 ppm	48 ppm	156 ppm	156 ppm
HC value after conditioning	67 ppm	4 ppm	16 ppm	3 ppm	6 ppm	20 ppm
Viscosity before conditioning	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s
Viscosity after conditioning	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s

\* Comparative Example

Table 2

	Example 7	Example 8	Example 9	Example 10	Example 11*	Example 12
Organic isocyanate	isophorone diisocyanate (IPDI)	isophorone diisocyanate (IPDI)	triisocyanato-nonane (TIN)	triisocyanato-nonane (TIN)	triisocyanato-nonane (TIN)	isophorone diisocyanate (IPDI)
Alcohol used	n-butanol	methanol	n-butanol	n-butanol	-	2-butanol
Wt.% of alcohol	1	1	2.4	4	-	1
Temperature	220°C	220°C	200°C	200°C	200°C	220°C
Reaction time [h]	6	6	6	6	6	6
HC value before conditioning	156 ppm	156 ppm	2300 ppm	2300 ppm	2300 ppm	156 ppm
HC value after conditioning	5 ppm	3 ppm	161 ppm	122 ppm	800 ppm	79 ppm
Viscosity before conditioning	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s
Viscosity after conditioning	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s

\* Comparative Example

Table 3

	Example 13*	Example 14	Example 15	Example 16*	Example 17
Organic isocyanate	isophorone diisocyanate (IPDI)	isophorone diisocyanate (IPDI)	isophorone diisocyanate (IPDI)	4,4'-diisocyanato-diphenylmethane	4,4'-diisocyanato-diphenylmethane
Alcohol used	tert.-butanol	glycerol	n-butanol	-	n-butanol
Wt. % of alcohol	1	1	2	-	1
Temperature	220°C	200°C	220°C	220°C	220°C
Reaction time [h]	6	6	2	6	6
HC value before conditioning	156 ppm	156 ppm	156 ppm	391 ppm	391 ppm
HC value after conditioning	10 ppm	33 ppm	11 ppm	151 ppm	5 ppm
Viscosity before conditioning	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s
Viscosity after conditioning	1850 mPa.s	75 mPa.s	< 50 mPa.s	< 50 mPa.s	< 50 mPa.s

\* Comparative Example

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Comparative Examples 1, 11 and 16 show that without the addition of a compound corresponding to Formula (I), insufficient purification of the isocyanate occurs, which is demonstrated by a relatively high HC value after conditioning. In contrast, very low HC values are achieved by adding even a small amount of a compound in accordance with Formula (I). (See Example 2.)

Comparative Example 13 shows an unacceptably large increase in viscosity when using tert.-butanol in accordance with DD 288 595. When a compound corresponding to Formula (I) was used, the viscosity remained substantially lower. (See Example 15)

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

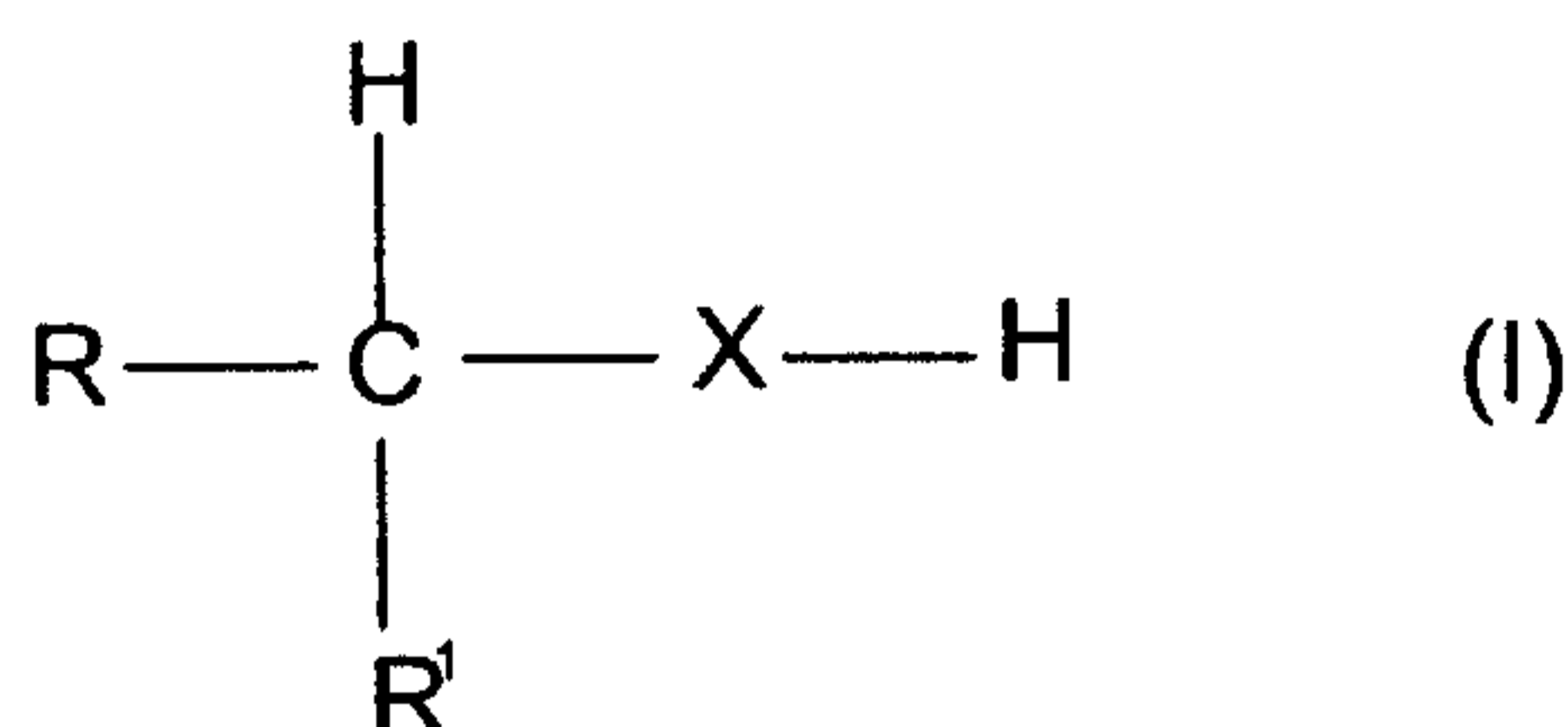
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CLAIMS:

1. A process for purifying an organic isocyanate comprising  
 a) adding a compound corresponding to Formula (I)

5



in which

10

X represents O or S and

R and R<sup>1</sup> independently, represent H, or a C<sub>1</sub>-C<sub>36</sub>-alkyl, C<sub>6</sub>-C<sub>36</sub>-aryl, C<sub>3</sub>-C<sub>36</sub>-cycloalkyl or C<sub>7</sub>-C<sub>36</sub>-aralkyl group, wherein the groups R and R<sup>1</sup> may be linked via a ring system and also either primary and secondary X-H groups or R and R<sup>1</sup> may also contain other functional groups which do not react with an isocyanate group, to the isocyanate to be purified in an amount of from about 0.01 to about 10 wt.%, based on the weight of the isocyanate,

15

20

- b) heating the product of a) for at least 5 minutes at a temperature of from about 100 to about 250°C, and  
 c) conducting at least one step selected from (i) stripping the product of b) with an inert gas or (ii) purifying the product of b) by distillation or (iii) purifying the product of b) by extraction.

25

2. The process of Claim 1 in which a solvent having no groups which are reactive with isocyanate groups is present during step b)

3. The process of Claim 1 in which step b) is carried out without a solvent.

30

4. The process of Claim 1 in which step b) is carried out at elevated pressure.

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5. The process of Claim 1 in which step b) is carried out at reduced pressure.
6. The process of Claim 1 in which steps b) and c)(i) are conducted simultaneously.
- 5 7. The process of Claim 1 in which step b) is substantially completed before step c) is carried out.
8. The process of Claim 1 in which the compound corresponding to Formula (I) is a primary alcohol.
9. The process of Claim 1 in which the compound  
10 corresponding to Formula (I) is n-butanol.
10. The process of Claim 1 in which step c) comprises stripping the product of b) with an inert gas and purification of the product of b) by distillation.