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(72) Inventeur/Inventor:
MECKEL, WALTER, DE
(73) Propriétaire/Owner:
BAYER AKTIENGESELLSCHAFT, DE
(74) Agent: FETHERSTONHAUGH & CO.

(54) Titre : ADHESIFS POUR BOIS A BASE DE PREPOLYMERES A TERMINAISON ISOCYANATE
(54) Title: WOOD ADHESIVES BASED ON ISOCYANATE-TERMINATED PREPOLYMERS

(57) **Abrégé/Abstract:**

The present invention provides a one-component wood adhesive, especially for the adhesive bonding of load-bearing components, based on isocyanate-terminated prepolymers. The adhesive possesses an improved water resistance. It has now been found that fillers based on polyadducts of, for example, toluene diisocyanates and hydrazine hydrate (polyhydrazodicarboxamides) make a positive contribution to the wet strength of wood. Since hydrazodicarboxamide structures are suitable for the formation of hydrogen bonds, the more likely expectation would have been of a certain hydrophilicity and hence poorer wet strengths. The present invention provides for the use of adhesives based on isocyanate-terminated prepolymers having an isocyanate content of 8 to 20% by weight, comprising: (a) at least one organic polyisocyanate; (b) at least one organic polyhydroxyl compound in the form of a dispersion comprising reaction products of: (i) organic polyisocyanates, with (ii) primary or secondary amino-containing polyamines, hydrazines or hydrazides, in a (iii) polyether containing at least two hydroxyl groups and having a molecular weight range from 500 to 12 000; and (c) if desired, auxiliaries and additives, for adhesively bonding wood substrates.



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ABSTRACT

The present invention provides a one-component wood adhesive, especially for the adhesive bonding of load-bearing components, based on isocyanate-terminated prepolymers. The adhesive possesses an improved water
5 resistance. It has now been found that fillers based on polyadducts of, for example, toluene diisocyanates and hydrazine hydrate (polyhydrazodicarboxamides) make a positive contribution to the wet strength of wood. Since hydrazodicarboxamide structures are suitable for the formation of hydrogen bonds, the more likely expectation would have been of a certain
10 hydrophility and hence poorer wet strengths. The present invention provides for the use of adhesives based on isocyanate-terminated prepolymers having an isocyanate content of 8 to 20% by weight, comprising: (a) at least one organic polyisocyanate; (b) at least one organic polyhydroxyl compound in the form of a dispersion comprising reaction products of: (i) organic polyisocyanates, with (ii)
15 primary or secondary amino-containing polyamines, hydrazines or hydrazides, in a (iii) polyether containing at least two hydroxyl groups and having a molecular weight range from 500 to 12 000; and (c) if desired, auxiliaries and additives, for adhesively bonding wood substrates.

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WOOD ADHESIVES BASED ON ISOCYANATE-TERMINATED
PREPOLYMERS

The present invention relates to the use of isocyanate-
5 terminated prepolymers as wood adhesives.

Adhesives based on phenol- or resorcinol-formaldehyde
or melamine-formaldehyde condensates are known and are
used for the adhesive bonding of wood, particularly for
10 high-load, long-lived wood structures (e.g.
EP-A 0 879 270). The reaction of the aqueous curing
agent mixture with the melamine resin is a
polycondensation, which releases water as the polymer
builds. For the reaction to proceed reproducibly,
15 therefore, the wood is required to meet strict
conditions on its water content.

In the case of high-load wood structures, such as load-
bearing components, for example, exacting requirements
20 are imposed on the mechanical strength of the
components. For example, the strength of the bond
should still be sufficiently high even after many years
under the effects of weathering.

25 The general service properties of adhesives are
determined by compliance with standards, such as
DIN EN 204, durability class D4 or WATT 91 (Wood
Adhesives Temperature Test), for example.

30 The gluing of wood with polyurethane adhesives, both as
one-component and as two-component systems, has been
known for a long time and is described in the journal
"Ahäsion - kleben&dichten", 41, 1-2/97, pp. 37-38
(1997). One-component systems are particularly suitable
35 for wood substrates, since the natural moisture content
of the wood ensures the availability of sufficient
water as a reactant. This removes the need for precise
monitoring of the water content or, as is usual with
many water-impermeable substrates, for the substrate

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surfaces to be sprayed with a water mist in order to ensure a complete reaction.

However, a disadvantage found with both one-component
5 and two-component systems is that when low-viscosity polyisocyanates are employed they migrate into the wood in the pressing operation. Although this results in a good bond between adhesive and wood, excessive migration is accompanied by an uncontrolled shift in
10 the NCO/OH ratio, this ratio being important for the building of the polymer. As a result, the adhesive is depleted of polyisocyanate in the joint, and in extreme cases incorrect bonds may occur.

15 In order to ensure an adequate concentration of adhesive in the joint, it is possible to use more viscous systems, but these may cause problems during application. Another possibility is to add fillers. Suitable fillers are, for example, organic fillers;
20 mineral fillers are not very suitable since they tend readily toward sedimentation and, in the case of mechanical conveying, can lead to increased abrasion levels in the complex pump and metering systems.

25 As organic fillers it is possible, for example, to use wood flour, cellulose fibers, but also polymer fibers. Polymer fibers in the form of short microfibers additionally act as a thixotropic additive. Particularly suitable fillers are dispersions, prepared
30 in situ, of polyureas and/or polyhydrazodicarboxamides in hydroxyl-containing polyethers, which are used widely to produce polyurethane foams with a heightened compressive strength (e.g. DE-A 25 13 815).

35 For flexible adhesive bonds with excellent cohesive strength use is made, in DE-A 27 19 720, for example, of both one-component and two-component polyurethane adhesives based on organic polyisocyanates and dispersions of polymers in organic hydroxyl compounds.

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A substantial disadvantage of glued wood structures is the susceptibility of the adhesive to moisture, leading to weakening of the adhesive film, which limits the use of glued wood structures in permanently humid environments. The consequence is that, in the dry state, substantial adherend failure of the wood is often to be found, while cohesive failure is observed in the course of prolonged water storage and/or in the boiling test.

10

The present invention provides a one-component wood adhesive, especially for

the adhesive bonding of load-bearing components, based on isocyanate-terminated prepolymers, said adhesive
15 possessing an improved water resistance.

It has now surprisingly been found that fillers based on polyadducts of, for example, tolylene diisocyanates and hydrazine hydrate (polyhydrazodicarboxamides) make
20 a positive contribution to the wet strength of wood. Since hydrazodicarboxamide structures are suitable for the formation of hydrogen bonds, the more likely expectation would have been of a certain hydrophilicity and hence poorer wet strengths.

25

The present invention accordingly provides for the use of adhesives based on isocyanate-terminated prepolymers having an isocyanate content of 8 to 20% by weight, comprising

30

a) at least one organic polyisocyanate,
b) at least one organic polyhydroxyl compound in the form of a dispersion comprising reaction products of

35

i) organic polyisocyanates with
ii) primary and/or secondary amino-containing polyamines and/or hydrazines and/or hydrazides in a
iii) polyether containing at least two hydroxyl groups and having a molecular weight range

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from 500 to 12 000, and
c) if desired, auxiliaries and additives

for adhesively bonding wood substrates.

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The isocyanate-terminated prepolymer preferably has an NCO content of from 10 to 18% by weight.

10 The reaction products b) used in accordance with the invention are polyureas and/or polyhydrazo-dicarboxamides, the amount of which should not fall below 2%, preferably 5%, by weight in the isocyanate-terminated prepolymer. Their fraction lies between 2 to 25%, preferably between 5 to 15%, by weight based on
15 the total amount of NCO prepolymer.

Suitable diisocyanates (i) for preparing the dispersed polyadducts are, for example, hexamethylene diisocyanate, 2,4-diisocyanatotoluene, 2,6-diisocyanatotoluene, and the isomer mixtures thereof, 3,3,5-trimethyl-5-isocyanatomethylcyclohexyl isocyanate or 4,4'-diphenylmethane diisocyanate, where appropriate in a mixture with 2,4'-MDI and its higher oligomers. Preference is given to the mixture of 2,4- and 2,6-di-
20 isocyanatotoluene in a ratio of 80 to 20.
25

Suitable synthesis components (ii) containing groups reactive toward isocyanate groups are, for example, primary and/or secondary aliphatic, araliphatic, cyclo-
30 aliphatic and aromatic amines with a functionality of two and/or more, such as ethylenediamine, hexamethylenediamine, trimethyldiaminohexane, N,N'-dimethyleneethylenediamine, higher homologs of ethylenediamine, such as diethylenetriamine, homologs of
35 propylenediamine, such as dipropylenetriamine, piperazine, triazine, 4-aminobenzylamine, 4,4'-diaminodicyclohexylmethane and -propane, 1,4-diaminocyclohexane, phenylenediamines, condensates of aniline and formaldehyde, tolylenediamines, and bisaminomethyl-

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benzenes. Likewise suitable is hydrazine, and also mono- or N,N'-disubstituted hydrazines, and hydrazides, such as hydrazides of dibasic or polybasic carboxylic acids, for example. Preference is given to hydrazine
5 hydrate.

Suitable polyethers (iii) containing at least two hydroxyl groups include polyadducts of propylene oxide and/or ethylene oxide with di- and trifunctional
10 initiators or mixtures thereof such as, for example, water, 1,2-propylene glycol, trimethylolpropane, glycerol, pentaerythritol or other polyhydroxyl compounds, such as, for example, polyetherpolyols based on tetrahydrofuran (polytetramethylene ether glycol) or
15 natural oils containing hydroxyl groups (e.g., castor oil). Naturally it is also possible to use any desired mixtures of such polyhydroxyl compounds.

The solids content of the dispersion b) of polyureas
20 and/or polyhydrazodicarboxamides in hydroxyl-containing polyethers is between 5 and 40% by weight, preferably between 10 and 25% by weight.

The fine, sedimentation-stable polyurea and/or poly-
25 hydrazodicarboxamide particles introduced as dispersions in hydroxyl-containing polyethers have a size of from 0.01 to 10, preferably from 0.01 to 1 μm . The viscosities of such filler-containing polyols at 25°C and a solids content of 20% by weight are less than
30 10 000, preferably less than 3 000 mPa*s.

In one preferred embodiment of the use in accordance with the invention the dispersion b) used comprises the reaction products of

- 35 - 16.9 parts by weight of a mixture of 2,4- and 2,6-diisocyanatotoluene (i) in a ratio of 80 to 20 with
- 4.85 parts by weight of hydrazine hydrate (ii) in 80 parts by weight of a polypropylene ether polyol

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(iii) having a functionality greater than 2 and an ethoxyethylene group content of from 0 to 30% preferably from 5 to 20% by weight and a hydroxyl number of from 20 to 56, preferably from 30 to 40 mgKOH/g.

The filled polypropylene ether polyol used in accordance with the invention is sold, for example, by the company Bayer AG in Leverkusen under the trade name Baycoll BT 5028.

Suitable polyisocyanates for synthesizing the isocyanate-terminated prepolymers are the aliphatic, cycloaliphatic, aromatic and heterocyclic polyisocyanates known from polyurethane chemistry, as described, for example, by W. Siefgen in Justus Liebigs Annalen der Chemie, 562, pages 75 to 136. Further suitable polyisocyanates are those polyisocyanates which possess, for example, isocyanurate, biuret, uretdione or carbodiimide groups. Polyisocyanates of this kind may have high functionalities, of more than 3, for example.

Preferred diisocyanates are 2,4- and/or 2,6-diisocyanatotoluene and also 2,4'- and/or 4,4'-diisocyanatodiphenylmethane or polyisocyanates as obtained by phosgenating aniline/formaldehyde condensates, which are known as polymeric MDI (P-MDI) and constitute a mixture of the monomeric 2,2'- and also 2,4'- and 4,4'-diphenylmethane diisocyanates with higher oligomers (polydiphenylmethane polyisocyanates). It is also possible to use mixtures of the monomeric diphenylmethane diisocyanates and P-MDI.

To prepare the NCO prepolymer the polymer dispersion is reacted with the organic polyisocyanate, which is subsequently processed as an adhesive which cures under the influence of moisture.

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- In the preparation of the NCO prepolymer there are from 3 to 30, preferably, from 5 to 20 isocyanate groups for each isocyanate-reactive group. The fraction of the polyol component b) in the finished NCO prepolymer is between 20 to 75% by weight, preferably between 30 to 60% by weight. The fraction of the polyisocyanate component a) is between 80 to 25% by weight, preferably between 70 to 40% by weight.
- 10 To prepare the prepolymers, in general, the excess component, the polyisocyanate a), is charged to the reactor at temperatures from 50 to 70°C and the polyol component b) is added at a rate such that the reactor temperature does not rise above 80°C. In principle it is also possible to mix the polyisocyanates a) and the polyols b) intensively with one another by way of a mixer (e.g., a static mixer or dynamic mixer or high-pressure nozzles) and, in doing so, to bring them to reaction.
- 20 Preferred prepolymers are obtained with organic polyisocyanates a) having a fraction of from 0 to 60%, preferably 5 to 40%, by weight of difunctional 2,4'-MDI and a fraction of higher oligomers having the functionality greater than 2 of from 0 to 50%, preferably 0 to 40% by weight. The 2,4'-MDI fraction in particular contributes to increased storage stability of the prepolymers.
- 25
- 30 In principle the possibility exists, for the preparation of the NCO prepolymers for use in accordance with the invention, either
- (I) to employ directly a 2,4'-MDI-containing organic polyisocyanate a) having an oligomeric fraction of from 20 to 60% by weight (P-MDI) or
- 35 (II) first to conduct the reaction with a pure diisocyanate which contains a 2,4'-MDI content of from 40 to 60% by weight until an NCO content of

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from 8 to 11% by weight is reached and then to add a P-MDI having an oligomeric fraction of up to 70% by weight so that the NCO content established in the mixture is from 14 to 18% by weight.

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The prepolymer prepared according to (II) has a lower viscosity compared with the prepolymer obtained according to (I).

10 The NCO prepolymers prepared in this way have viscosities at 25°C of less than 20 000, preferably less than 10 000 mPa*s.

Furthermore, for example, the additional use of up to
15 20 parts by weight of amine-initiated polypropylene/ethylene ether glycols in component b) may be advantageous, since they give the prepolymers an accelerated reaction with atmospheric moisture. Mention may be made here in particular of ethylenediamine- or
20 ammonia-initiated polypropylene ether polyols having an OH number of from 40 to 200 mgKOH/g. An accelerated reaction of this kind with atmospheric moisture can of course also be achieved with the customary catalysts common in polyurethane chemistry, examples being
25 tertiary amines, such as diazabicyclooctane, dimorpholinodiethyl ether or metal catalysts such as dibutyltin dilaurate, in amounts of from 0.005 to 0.5% by weight based on prepolymer.

30 The prepolymers may also be provided with the customary additives, such as thickeners, e.g., superficially hydrophobicized Aerosils, short fibers such as Kevlar pulp or similar microfibers for imparting thixotropy, for example. It is additionally possible to add further
35 additives, where appropriate, to the adhesives used in accordance with the invention, in order to modify them, such as natural or synthetic resins, pigments or aging inhibitors.

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The adhesives used in accordance with the invention are notable for the fact that on storage in water at 20°C for several days they still exhibit sufficient adherend failure. They are therefore particularly suitable for bonding high-load components, such as load-bearing wood structures.

Examples

10 Prepolymer preparation

The polyisocyanates are introduced at 70°C and the dewatered polyols (water content < 0.05%) are added at a rate such that the temperature is situated in the range between 60 and 80°C.

When a constant NCO value is obtained the prepolymer is adjusted, where appropriate by adding dibutyltin dilaurate, to a film dry time of about 30 to 60 minutes.

The film dry time here is determined using the BK Drying Recorder from the Mickle Laboratory Engineering Co. Ltd. (type 10) (measurement conditions: 23°C, 50% humidity, 100 mm adhesive film and 10 g weight).

Polyols

Polyol I TM Baycoll BT 5028 (Bayer AG, Leverkusen): polypropylene ether polyol having an OH number of 28.6 mgKOH/g obtained in accordance with DE-A 2513815. The polyether polyol contains 20% by weight of a reaction product of tolylene diisocyanate hydrazine hydrate in the form of a sedimentation-stable dispersion in trifunctional polyether of OH number

Polyol II Baycoll BT 5035 (Bayer AG, Lev

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polypropylene ether glycol of OH number 35 mgKOH/g initiated on glycerol ethylene oxide content about 20% by weight.

5 Polyol III Baycoll BD 2060 (Bayer AG, Leverkusen): polypropylene ether glycol of OH number 56 mgKOH/g.

10 Polyol IV Baycoll BD 1110 (Bayer AG, Leverkusen): polypropylene ether glycol of OH number 112 mgKOH/g.

15 Polyol V Baycoll ET 3059 (Bayer AG, Leverkusen): amine-initiated polypropylene ether glycol of OH number 56 mgKOH/g.

20 Polyol VI ArcolTM 1096 (Lyondell, USA): polypropylene ether polyol having an OH number of 28 mgKOH/g; contains 40% by weight of a styrene-acrylonitrile polymer in the form of a fine, sedimentation-stable dispersion in a trifunctional polyether.

25 Polyol VII TerathaneTM 2000 (Dupont, Europe): polytetramethylene ether glycol of OH number 112 mgKOH/g.

Polyisocyanates

30 Iso-I DesmodurTM VP KA 8616 (Bayer AG, Leverkusen) (monomeric MDI): mixture of 54% by weight 2,4'-MDI and 46% by weight 4,4'-MDI.

35 Iso-II Desmodur VKS 20 F (Bayer AG, Leverkusen) (polymeric MDI) having an NCO content of 31.6% and a polymer fraction of 50% by weight.

Iso-III Desmodur VK 5 (Bayer AG, Leverkusen)

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(polymeric MDI) having an NCO content of 32.6% and a polymer fraction of 10% by weight and a 2,4'-MDI content of 45%.

- 5 Iso-IV Desmodur VK 10 (Bayer AG, Leverkusen)
 (polymeric MDI) having an NCO content of
 31.5% and a polymer fraction of 38% by
 weight and a 2,4'-MDI content of 17%.

10 **Example 1 (inventive)**

From 589 g of Pol-1 and 611 g of ISO-IV an NCO prepolymer is obtained having an NCO content of 14.67% and a viscosity of 6 500 mPa*s at 23°C.

15

With 0.01% % by weight dibutyltin dilaurate a film dry time (FDT) of 45 minutes is obtained.

Example 2 (comparative)

20

From 292 g of Pol-II, 291 Pol-VI g and 617 g of ISO-IV an NCO prepolymer is obtained having an NCO content of 15.16% and a viscosity of 7 600 mPa*s at 23°C.

- 25 With 0.01% % by weight dibutyltin dilaurate a film dry time (FDT) of 37 minutes is obtained.

Example 3 (comparative)

- 30 From 152 g of Pol-III, 280 g Pol-V and 400 g of ISO-II and 170 g of Iso-III an NCO prepolymer is obtained having an NCO content of 16.10% and a viscosity of 5 600 mPa*s at 23°C.

- 35 The film dry time (FDT) is 56 minutes.

Example 4 (comparative)

From 222 g of Pol-IV, 222 g Pol-V and 556 g of ISO-I an

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NCO prepolymer is obtained having an NCO content of 15.60% and a viscosity of 1 950 mPa*s at 23°C.

The film dry time (FDT) is 58 minutes.

5

Example 5 (comparative)

From 490 g of Pol-III and 357 g Iso-II and 170 g of Iso-III an NCO prepolymer is obtained having an NCO content of 13.40% and a viscosity of 6 500 mPa*s at 23°C.

Following addition of 0.2% of tosyl isocyanate and 0.25% of dibutyltin dilaurate a film dry time (FDT) of 43 minutes is obtained.

Example 6 (comparative)

From 371 g of Pol-VII, 15 g of trimethylolpropane and 614 g of ISO-I and 170 g of Iso-II an NCO prepolymer is obtained having an NCO content of 16.10% and a viscosity of 3 100 mPa*s at 23°C.

The film dry time (FDT) following addition of 0.015% of DBTL is 42 minutes.

Wood bonds

The adhesives were made available to the Institut für Fenstertechnik [Institute for window engineering] e.V. in Rosenheim for testing to DIN EN 204, durability class D4 and the WATT 91 test.

In each case, 20 test specimens in accordance with the standard were produced and tested.

The results obtained were as follows:

Table 1: Test results

Example	1	2	3	4	5	6
Testing	N/mm ² / % ADF	N/mm ² / % ADF	N/mm ² / % ADF	N/mm ² / % ADF	N/mm ² / % ADF	N/mm ² / % ADF
Storage 1	10.83 100	11.56 100	10.46 100	11.53 100	10.80 100	10.52 100
Storage 3	7.98 60-90	7.03 0	5.12 0	5.61 0	5.89 0	4.97 0
Storage 5	4.87 0-100	6.73 0	6.43 0	5.96 0	6.55 0-75	7.23 0
Storage 6	12.43 100	12.18 100	10.48 100	10.02 100	10.08 100	12.88 100
WATT 91	11.74 100	14.02 50-100	12.71 100	10.00 0-30	12.84 0-100	12.30 100

Storage 1: 7 days under standard conditions (20°C and 65% relative atmospheric humidity, RAH).

Storage 3: 7 days under standard conditions; 4 days in cold water (20°C)

Storage 5: 7 days under standard conditions; 6 hours in boiling water; 2 hours in cold water

Storage 6: 7 days under standard conditions; 6 hours in boiling water; 2 hours in cold water; 7 days standard conditions

WATT 91: 1 hour of storage at 80°C and tear while hot

N/mm² Bond strength in the tensile shear test at an advancing speed of 50 mm/min.

ADF: Adherend failure in % of the bond area

It can be seen from the table that, although DIN EN 204 durability D4 is met by all the prepolymers, only the NCO prepolymer of the invention still exhibits a considerable adherend failure when stored for a long time in water (storage 3).

Furthermore, the prepolymer of the invention passes the heat test (WATT 91) with very good performance.

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CLAIMS:

1. Use of an adhesive based on an isocyanate-terminated prepolymer having an isocyanate content of 8 to 20% by weight, comprising:
 - (a) at least one organic polyisocyanate;
 - 5 (b) at least one organic polyhydroxyl compound in the form of a dispersion comprising a reaction product of:
 - (i) an organic polyisocyanate, with
 - (ii) a primary or secondary amino-containing polyamine, a hydrazine or a hydrazide, in a
 - 10 (iii) polyether containing at least two hydroxyl groups and having a molecular weight range from 500 to 12 000; and
 - (c) optionally, an auxiliary and an additive, for adhesively bonding load-bearing wood components possessing an improved water resistance.
2. The use as claimed in claim 1, wherein the reaction product present
15 in the dispersion (b) is a polyurea or a polyhydrazodicarboxamide whose fraction is 2 to 25% by weight, based on the total amount of the isocyanate-terminated prepolymer.
3. The use as claimed in claim 2, wherein polyurea or polyhydrazodicarboxamide particles have a size of from 0.01 to 10 μm .
- 20 4. The use as claimed in any one of claims 1 to 3, wherein the dispersion (b) has a solids content of from 5 to 40% by weight.
5. The use as claimed in any one of claims 1 to 4, wherein the dispersion (b) comprises a reaction product of 16.9 parts by weight of a mixture of 2,4- and 2,6-diisocyanatotoluene (i) in a ratio of 80 to 20 with 4.85 parts by weight

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of hydrazine hydrate (ii) in 80 parts by weight of a polypropylene ether polyol (iii) having a functionality greater than 2.

6. The use as claimed in any one of claims 1 to 5, wherein the polyether (iii) is a polypropylene ether polyol which has an ethoxyethylene group
5 content of from 0 to 30% by weight and a hydroxyl number of from 20 to 56 mgKOH/g.

7. The use as claimed in any one of claims 1 to 6, wherein the organic polyisocyanate (a) is obtained by phosgenating an aniline/formaldehyde condensate, having a fraction of from 0 to 60% by weight of difunctional 2,4'-MDI
10 and a fraction of higher oligomers having a functionality greater than 2 of from 0 to 50% by weight, wherein the sum of the fractions is 100%.