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(54) Title: WATER-EMULSIFIABLE POLYISOCYANATE COMPOSITION COMPRISING A FRAGRANT WITH AT LEAST ONE HYDROXYL AND/OR ALDEHYDE GROUP

(57) Abstract: An aqueous composition comprises a water-emulsifiable polyisocyanate (A), the water-emulsifiable polyisocyanate (A) being a reaction product of a polyisocyanate (B) with a compound (C) which contains at least one sulfonic acid group or its anion, and at least one isocyanate-reactive group. The composition further comprises a fragrant (D1) with at least one hydroxyl and/or aldehyde group. It has been found that the addition of the fragrant (D1) can mask unpleasant odors of the composition. This is particularly the case when organic co-solvents such as propylene glycol-n-butyl ether and/or 3-methoxy-1-butyl acetate are used. The storage stability and performance of the polyisocyanates are not affected by the addition of the fragrant (D1). Further aspects of the invention are the use of a composition according to the invention as an adhesive, a coating or an impregnating material and a substrate coated with a composition according to the invention.



Water-emulsifiable polyisocyanate composition comprising a fragrant with at least one hydroxyl and/or aldehyde group

The present invention relates to an aqueous composition comprising a water-emulsifiable polyisocyanate (A), the water-emulsifiable polyisocyanate (A) being a reaction product of a polyisocyanate (B) with a compound (C) which contains at least one sulfonic acid group or its anion,  
5 and at least one isocyanate-reactive group. Further aspects of the invention are the use of a composition according to the invention as an adhesive, a coating or an impregnating material and a substrate coated with a composition according to the invention.

Water-emulsifiable polyisocyanates have gained importance for various fields of use in recent years.  
10 They are currently used in particular as cross-linking components for high-quality water-dilutable two-component polyurethane paints (2C PU paints) or as an additive for aqueous dispersion adhesives, are used for cross-linking aqueous dispersion in textile finishing or formaldehyde-free textile printing inks and moreover are also suitable, for example, as auxiliary substances for wet-strength finishing of paper (cf. e.g. EP 0 959 087 A1 and literature cited herein).

15 US 5,583,176 discloses water-emulsifiable polyisocyanates, containing aliphatic, cycloaliphatic or aromatic polyisocyanates and reaction products of the abovementioned polyisocyanates with compounds which contain at least one group called a sulfo group, and at least one isocyanate-reactive group.

A specific example of modified polyisocyanates is given in US 2004/034162 A1 which discloses  
20 modified polyisocyanates obtainable by reaction of polyisocyanates with 2-(cyclohexylamino)-ethanesulfonic acid and/or 3-(cyclohexylamino)-propanesulfonic acid.

The water-emulsifiable polyisocyanates may sometimes have an unpleasant odor either as an inherent property or due to impurities or additional components. This may especially be the case when the water-emulsifiable polyisocyanates are supplied in the form of a solution with an organic  
25 co-solvent.

The present invention has the object of providing water-borne polyisocyanate compositions which are more acceptable to a professional user or a private customer due to an improved smell.

According to the present invention this object is achieved by an aqueous composition comprising a water-emulsifiable polyisocyanate (A), the water-emulsifiable polyisocyanate (A) being a reaction  
30 product of a polyisocyanate (B) with a compound (C) which contains at least one sulfonic acid group

or its anion, and at least one isocyanate-reactive group. The composition further comprises a fragrant (D1) with at least one hydroxyl and/or aldehyde group.

Since the fragrances useful in this respect contain OH or aldehyde groups it has been thought that they could not be introduced into water-emulsifiable polyisocyanate compositions without adversely influencing the performance or the storage stability of the polyisocyanate. It has been surprisingly found that this is not the case.

Therefore better smelling (or less off-putting smelling) storage-stable cross-linkers are provided. An additional advantage is that the OH- or aldehyde-functional fragrances (D1) may also be incorporated into a polyurethane matrix under appropriate conditions. This is advantageous if, for example, it is not desirable for a final coating or an adhesive to have an odor of its own.

Examples for polyisocyanates (B) as a starting material for forming water-emulsifiable polyisocyanates (A) include aliphatic diisocyanates such as tetramethylene diisocyanate, hexamethylene diisocyanate (1,6-diisocyanatohexane), octamethylene diisocyanate, decamethylene diisocyanate, dodecamethylene diisocyanate, tetradecamethylene diisocyanate, trimethylhexane diisocyanate or tetramethylhexane diisocyanate, cycloaliphatic diisocyanates such as 1,4-, 1,3- or 1,2-diisocyanatocyclohexane, 4,4'-di(isocyanatocyclohexyl)methane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate) or 2,4-, or 2,6-diisocyanato-1-methylcyclohexane and also aromatic diisocyanates such as 2,4- or 2,6-tolylene diisocyanate, tetramethylxylylene diisocyanate, p-xylylene diisocyanate, 2,4'- or 4,4'-diisocyanatodiphenylmethane, 1,3- or 1,4-phenylene diisocyanate, 1-chloro-2,4-phenylene diisocyanate, 1,5-naphthylene diisocyanate, diphenylene 4,4'-diisocyanate, 4,4'-diisocyanato-3,3'-dimethyldiphenyl, 3-methyldiphenylmethane 4,4'-diisocyanate or diphenyl ether 4,4'-diisocyanate. Mixtures of the diisocyanates mentioned can also be present. Hexamethylene diisocyanate and isophorone diisocyanate are preferred.

Suitable customary more highly functionalized polyisocyanates are, for example, triisocyanates such as 2,4,6-triisocyanatotoluene or 2,4,4'-triisocyanatodiphenyl ether or the mixtures of di-, tri- and higher polyisocyanates which are obtained by phosgenation of appropriate aniline/formaldehyde condensates and represent polyphenyl polyisocyanates having methylene bridges.

Also suitable are customary aliphatic more highly functionalized polyisocyanates of the following groups:

(a) Isocyanurate-containing polyisocyanates of aliphatic and/or cycloaliphatic diisocyanates. Particularly preferred in this context are the corresponding isocyanato isocyanurates based on

hexamethylene diisocyanate and isophorone diisocyanate. The isocyanurates are, in particular, simple trisisocyanatoalkyl or tris-isocyanatocycloalkyl isocyanurates which are cyclic trimers of the diisocyanates, or mixtures with their higher homologs containing more than one isocyanurate ring. The isocyanato isocyanurates in general have an NCO content of from 10 to 30% by weight, in particular 15 to 25% by weight, and a mean NCO functionality of from 2,6 to 4,5.

(b) Uretdione diisocyanates having aliphatically and/or cycloaliphatically bonded isocyanate groups, preferably derived from hexamethylene diisocyanate or isophorone diisocyanate. Uretdione diisocyanates are cyclic dimerization products of diisocyanates.

(c) Biuret-containing polyisocyanates having aliphatically bonded isocyanate groups, in particular tris(6-isocyanatohexyl)biuret or its mixtures with its higher homologs. These biuret-containing polyisocyanates in general have an NCO content of from 10 to 30 % by weight, in particular from 18 to 25% by weight, and a mean NCO functionality of from 3 to 4,5.

(d) Urethane- and/or allophanate-containing polyisocyanates having aliphatically or cycloaliphatically bonded isocyanate groups, as can be obtained, for example, by reaction of excess amounts of hexamethylene diisocyanate or of isophorone diisocyanate with simple polyhydric alcohols such as trimethylolpropane, glycerol, 1,2-dihydroxypropane or mixtures thereof. These urethane- and/or allophanate-containing polyisocyanates in general have an NCO content of from 12 to 20% by weight and a mean NCO functionality of from 2,5 to 3.

(e) Oxadiazinetriene-containing polyisocyanates, preferably derived from hexamethylene diisocyanate or isophorone diisocyanate. Such oxadiazinetriene-containing polyisocyanates can be prepared from diisocyanate and carbon dioxide.

(f) Uretonimine-modified polyisocyanates.

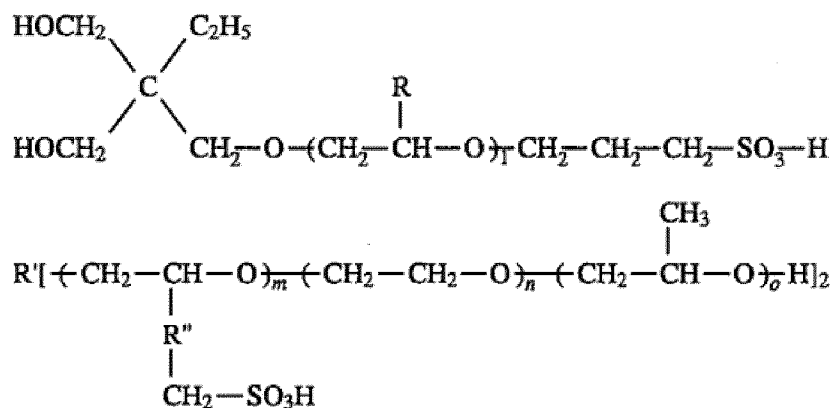
Aliphatic and cycloaliphatic polyisocyanates are particularly preferred. Hexamethylene diisocyanate and isophorone diisocyanate are very particularly preferred, in particular their isocyanurates and biurets.

For the preparation of the water-emulsifiable polyisocyanates (A), the above named polyisocyanates are reacted with compounds which contain at least one, preferably one, sulfonic acid group or its anion and at least one, preferably one, isocyanate-reactive group, e.g. a hydroxyl, mercapto or primary or secondary amino group (in short an NH group).

Such compounds are, for example, hydroxy- or aminosulfonic acids or alternatively hemiesters of sulfuric acid with OH or NH groups. Compounds containing a sulfonic acid group are preferred.

Hydroxysulfonic acids are also preferred. Hydroxysulfonic acids having an aliphatically bonded OH group are very particularly preferred. Examples of these are hydroxysulfonic acids and the tertiary ammonium and alkali metal salts derived therefrom having the following structures:

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where R=H or CH<sub>3</sub>; R' and R'' are divalent organic radicals, preferably having 1 to 20 C atoms; l=5 to 50; m=1 to 5; n=0 to 50 and o=0 to 50 (obtainable from Goldschmidt AG).

Furthermore, compounds which can be used are ammonium sulfobetaines, as can be obtained by quaternization of tertiary amines containing hydroxyl groups with propane sulfone.

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Adducts of bisulfites to olefinically unsaturated alcohols can also be used, as are described, for example, in DE-A-24 17 664, DE-A-24 37 218 and DE-A-24 46 440 and the references mentioned therein.

Specifically, 2-hydroxyethanesulfonic acid and 2-hydroxypropanesulfonic acid can also be used.

For the preparation of the water-dispersible polyisocyanates the polyisocyanates described above are reacted with the compounds which contain both sulfonic acid groups and isocyanate-reactive groups.

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The sulfonic acid-containing compounds can be employed either in their acid or their salt form. The higher molecular weight sulfo-containing compounds can be used in the form of their alkali metal salts, as the large organic radical has a sufficient solubility in the starting polyisocyanate. The alkali metal salts of the low molecular weight sulfo-containing compounds are in general not soluble in the reaction medium. In this case, it is advantageous to prepare the free acids according to generally known methods and either to employ them as such or in the form of their salts with tertiary amines. In the case where the free acid was used, the neutralization can either be carried out later by addition

of anhydrous bases, e.g. tertiary amines, to the water-emulsifiable polyisocyanate or by emulsification of the water-emulsifiable polyisocyanate in base-containing water.

It can be advantageous to use solvents which are inert to NCO in the synthesis, such as hydrocarbons, ketones, esters, amides or suitable lactams. The reaction is preferably carried out at  
5 from 20 °C to 150 °C; if appropriate with additional use of customary catalysts, e.g. dibutyltin dilaurate or diazabicyclooctane.

Examples for suitable fragrances (D1) include, under the proviso of having at least one hydroxyl and/or aldehyde group, compounds selected from the group comprising unsaturated or saturated, acyclic, monocyclic or bicyclic monoterpenes and sesquiterpenes, which may in each case be  
10 substituted with 1, 2, 3 or 4 identical or different substituents selected from the group comprising an -OH, oxo (=O or -O-), -O-C<sub>1-5</sub>-alkyl, -O-phenyl, -C(-O)-OH, -C(-O)-O-C<sub>1-5</sub>-alkyl, -C(-O)-O-phenyl, -O-C(-O)-C<sub>1-5</sub>-alkyl, -O-C(-O)-phenyl group and -CN, the alkyl and/or phenyl residue possibly being substituted with 1, 2 or 3 substituents selected from the group comprising OH, oxo (=O) and -O-C<sub>1-5</sub>-alkyl; phenyl or naphthyl compounds, which may in each case be substituted with 1, 2, 3, 4 or 5  
15 identical or different substituents selected from the group comprising a -C(-O)-H, -C(-O)-C<sub>1-5</sub>-alkyl, -C(-O)-phenyl, -OH, -C<sub>1-5</sub>alkyl, -C<sub>2-5</sub>alkenyl, -O-C<sub>1-5</sub>-alkyl, -O-C(-O)-C<sub>1-5</sub>-alkyl, -O-C(-O)-C<sub>2-6</sub>-alkylene, -O-C(-O)-phenyl, -O-C(-O)-OH, phenyl, -C(-O)-OH, -C(-O)-O-C<sub>1-5</sub>-alkyl, -C(-O)-O-C<sub>2-8</sub>-alkenyl, -C(-O)-O-phenyl, -C(-O)-O-C<sub>3-8</sub>-cycloalkyl, -CH-C(-C<sub>1-5</sub>-alkyl)(C(-O)-H), -NO<sub>2</sub> and -NH<sub>2</sub> group, the substituents in each case possibly being attached by way of a linear or branched C<sub>1-7</sub>  
20 alkylene or C<sub>2-5</sub> alkenylene bridge, which may in each case be substituted with 1, 2 or 3 identical or different substituents selected from the group comprising F, Cl, and Br; phenyl or naphthyl compounds, which may be condensed with 1 or 2 unsaturated or saturated 5- to 7-membered aliphatic rings, wherein the rings may in each case comprise 1, 2 or 3 heteroatom(s) selected from the group consisting of oxygen, nitrogen and sulfur as ring member(s) and be substituted with 1, 2,  
25 3, 4 or 5 identical or different substituents selected from the group comprising a -C<sub>1-5</sub>alkyl, -OH and -O-C<sub>1-5</sub>-alkyl group; and unsaturated or saturated, unsubstituted, linear, branched or cyclic esters, alcohols and aldehydes, which comprise 5 to 20, preferably 5 to 16, carbon atoms and optionally 1, 2 or 3 heteroatom(s) selected from the group consisting of oxygen and sulfur as chain link(s) or ring member(s).

30 Preferably the aqueous composition contains as fragrance (D1) at least one natural or nature-identical compound selected from the group consisting of benzaldehyde, benzyl alcohol, neral, citronellal, citronellol, farnesol, decanal, dihydrolinalool, dihydromyrcenol, dimethylphenylcarbinol, eucalyptol, geraniol, hydroxycitronellal, linalool, linalool oxide, methylnonylacetaldehyde, myrcenol,

nerol, phenylethyl alcohol, alpha-terpinol, beta-terpinol, alpha-amylcinnamaldehyde, amyl salicylate, cinnamyl alcohol, cinnamyl aldehyde, ethylvanillin, eugenol, iso-eugenol, piperonal, linal, nerolidol, patchouli alcohol, phenylhexanol, triethyl citrate, vanillin, dimethoxybenzaldehyde, hexylcinnamaldehyde and lylal® (3-and 4-(4-hydroxy-4-methyl-pentyl) cyclohexene-1-carboxaldehyde). More preferably the aqueous composition contains as fragrance (D1) at least one natural or nature-identical compound selected from the group consisting of benzaldehyde, benzyl alcohol, citronellol, farnesol, geraniol, alpha-terpinol, beta-terpinol, alpha-amylcinnamaldehyde, cinnamyl aldehyde, eugenol and iso-eugenol.

Further fragrances which may be present in the composition according to the invention are disclosed in David J. Rowe, Chemistry and Technology of Flavors and Fragrances, Taylor & Francis Group, 2004; Michael Edwards, Fragrances of the World 2005, Crescent House Pub., 2004 and David Pybus, The Chemistry of Fragrances, Royal Society of Chemistry, 1999. The corresponding disclosures are hereby deemed to be part of the present disclosure.

At least one naturally occurring mixture of fragrances may also be used as a fragrance (D1) for the composition according to the invention. In particular, at least one suitable fragrance or aroma additive mixture is selected from the group comprising rosemary oil, sandalwood oil, violet oil, lemon grass oil, lavender flower oil, eucalyptus oil, peppermint oil, chamomile oil, clove leaf oil, cinnamon oil, thyme oil, tea tree oil, cajeput oil, niaouli oil, manuka oil, citrus oil, mountain pine oil, jasmine oil, geranium oil, caraway oil, pine-needle oil, bergamot oil, turpentine oil, linalol oil, blood orange oil, cypress oil, silver fir oil, fennel oil, grapefruit oil, ginger oil, pine-needle oil, lavandin oil, lemon-grass oil, lime oil, mandarin oil, melissa oil, myrrh oil, patchouli oil, rosewood oil and thuja oil.

The aqueous mixture may further comprise fragrances (D2) selected from the group comprising unsaturated or saturated, acyclic, monocyclic or bicyclic monoterpenes and sesquiterpenes, which may in each case be substituted with 1, 2, 3 or 4 identical or different substituents selected from the group comprising an -OH, oxo (=O or -O-), -O-C<sub>1-5</sub>-alkyl, -O-phenyl, -C(-O)-OH, -C(-O)-O-C<sub>1-5</sub>-alkyl, -C(-O)-O-phenyl, -O-C(-O)-C<sub>1-5</sub>-alkyl, -O-C(-O)-phenyl group and -CN, the alkyl and/or phenyl residue possibly being substituted with 1, 2 or 3 substituents selected from the group comprising OH, oxo (=O) and -O-C<sub>1-5</sub>-alkyl. By way of example, the composition according to the invention may contain as fragrance (D2) limonene, myrcene, pinene, terpinene, selinene, camphene and cymene.

It is possible that the composition further comprises an aliphatic, cycloaliphatic or aromatic polyisocyanate (E) which is different from the water-emulsifiable polyisocyanate (A). This

polyisocyanate may be identical to or different than the polyisocyanate (B) used for the formation of the water-emulsifiable polyisocyanate (A). In such mixtures the polyisocyanates (A) take over the function of an emulsifier for the subsequently admixed content of non-hydrophilic polyisocyanates (E).

- 5 It is also possible that the composition according to the invention also comprises organic co-solvents. Examples for these co-solvents include esters, ethers and ketones. Then the added fragrant also has a safety benefit because it signals to the user of the composition that an organic and thus potentially flammable solvent is present.

The present invention will be further described in connection with various embodiments which may  
10 be combined freely unless the context clearly indicates otherwise.

In one embodiment of the composition according to the invention the composition further comprises propylene glycol-n-butyl ether and/or 3-methoxy-1-butyl acetate as an organic co-solvent.

- In another embodiment of the composition according to the invention the fragrant (D1) is preferably present in an amount of 0,1 weight-% to  $\leq 3$  weight-%, more preferably in an amount of 0,2 weight-%  
15 % to  $\leq 3$  weight-%, even more in an amount of 0,3 weight-% to  $\leq 2,5$  weight-%, based on the total amount of water-emulsifiable polyisocyanate (A).

In another embodiment of the composition according to the invention the combined amount of sulfonic acid groups and anions of sulfonic acid groups is  $\geq 0,03$  mol/kg to  $\leq 3$  mol/kg of water-emulsifiable polyisocyanate (A).

- 20 As already outlined above, in another embodiment of the composition according to the invention the compound (C) containing at least one sulfonic acid group or its anion and at least one isocyanate-reactive group is a hydroxysulfonic acid, an aminosulfonic acid or a hemiester of sulfuric acid with a hydroxyl group or a primary or secondary amino group.

- Preferably the compound (C) containing at least one sulfonic acid group or its anion and at least one  
25 isocyanate-reactive group is 2-(cyclohexylamino)-ethanesulfonic acid and/or 3-(cyclohexylamino)-propanesulfonic acid and/or anions or zwitterions of the aforementioned sulfonic acids. 2-(cyclohexylamino)-ethanesulfonic acid (CHES), 3-(cyclohexylamino)-propanesulfonic acid (CAPS) or any desired mixtures of these two aminosulfonic acids are suitable. These compounds are known, they are in crystalline form as zwitterionic substances, and have melting points above 300 °C. The  
30 preparation of CHES and CAPS is described, for example, in Bull. Soc. Chim. France 1985, 463



and in Z. Chem. 7, 151 (1967). The preparation of CAPS-modified polyisocyanates is mentioned in great detail in US 2004/034162 A1.

In another embodiment of the composition according to the invention the water-emulsifiable polyisocyanate (A) further comprises alkylene oxide units. The dispersability of polyisocyanates already modified with, for example, ethylene oxide polyether units is considerably improved by the modification with 2-(cyclohexylamino)-ethanesulfonic acid and/or 3-(cyclohexylamino)-propanesulfonic acid, so that the use of external emulsifiers or the use of high shear forces can be dispensed with, which considerably simplifies the preparation of the ready-to-use formulations. For this, a polyisocyanate is reacted with 2-(cyclohexylamino)-ethanesulfonic acid and/or 3-(cyclohexylamino)-propanesulfonic acid in the presence of polyalkylene oxide polyether alcohols containing ethylene oxide units and/or the polyisocyanates employed optionally already contain such units.

Preferably the alkylene oxide units are ethylene oxide units. For example, the content of ethylene oxide groups bonded within polyether chains (calculated as  $C_2H_2O$ ; molecular weight = 44 g/mol) may be > 0 weight-% to  $\geq 19,5$  weight-% with respect to the modified polyisocyanate (A). polyether chains may contain a statistical average of 5 to 55 ethylene oxide units.

The present invention is further directed to the use of a composition according to the invention as an adhesive, a coating or an impregnating material.

Another aspect of the present invention is a substrate coated with a composition according to the invention.

The polyisocyanate compositions according to the invention are particularly preferably used as cross-linking agents for paint binders or paint binder components which are dissolved or dispersed in water and have groups which are reactive towards isocyanate groups, in particular alcoholic hydroxyl groups, in the production of coatings using aqueous coating compositions based on such binders or binder components. The combining of the cross-linking agent, optionally in emulsified form, with the binders or binder components can be carried out here by simple stirring before processing of the coating compositions by any desired methods, using mechanical aids known to the expert or also using two-component spray guns.

In this connection, paint binders or paint binder components which may be mentioned by way of example are: polyacrylates which are dissolved or dispersed in water and contain hydroxyl groups, in particular those of the molecular weight range of 1000 to 10000 g/mol, which, with organic polyisocyanates as cross-linking agents, are valuable two-component binders, or optionally urethane-

modified polyester resins containing hydroxyl groups, of the type known from polyester and alkyd resin chemistry, which are dispersed in water. All binders which are dissolved or dispersed in water and contain groups which are reactive towards isocyanates are in principle suitable as reaction partners for the polyisocyanate mixtures according to the invention. These also include, for example, polyurethanes or polyureas which are dispersed in water and can be cross-linked with polyisocyanates on the basis of the active hydrogen atoms present in the urethane or urea groups.

The compositions according to the invention are in general used as cross-linking components for aqueous paint binders in those amounts which correspond to an equivalent ratio of NCO groups to groups which are reactive towards NCO groups, in particular alcoholic hydroxyl groups, of 0,5:1 to 2:1.

The polyisocyanate compositions according to the invention can also optionally be admixed in minor amounts to non-functional aqueous paint binders to achieve quite specific properties, for example as an additive to improve adhesion.

The polyisocyanates in the composition according to the invention can of course also be employed in a form blocked with blocking agents known per se from polyurethane chemistry, in combination with the abovementioned aqueous paint binders or paint binder components in the sense of aqueous one-component PU stoving systems. Suitable blocking agents are, for example, malonic acid diethyl ester, acetoacetic ester, acetone oxime, butanone oxime, epsilon-caprolactam, 3,5-dimethylpyrazole, 1,2,4-triazole, dimethyl-1,2,4-triazole, imidazole or any desired mixtures of these blocking agents.

Possible substrates for the aqueous coatings formulated with the aid of the polyisocyanate composition according to the invention include metal, wood, glass, stone, ceramic materials, concrete, rigid and flexible plastics, textiles, leather and paper, which can optionally also be provided with conventional primers before the coating.

The aqueous coating compositions which are formulated with the polyisocyanate compositions according to the invention and to which the conventional auxiliary substances and additives in the paint sector, such as e.g. flow auxiliaries, colored pigments, fillers, matting agents or emulsifiers, can optionally be added in general already have good paint properties on drying at room temperature.

However, they can of course also be dried under forced conditions at elevated temperature or by stoving at temperatures up to 260 °C.

Because of their emulsifiability in water, which allows a homogenous, particularly finely divided distribution in aqueous paint binders, the use of the polyisocyanates as cross-linking components for

aqueous polyurethane paints leads to coatings with outstanding optical properties, in particular high surface gloss, flow and high transparency.

In addition to the preferred use as cross-linking components for aqueous 2C PU paints, the polyisocyanates according to the invention are outstandingly suitable as cross-linking agents for  
5 aqueous dispersion adhesives, leather and textile coatings or textile printing pastes, as AOX-free papermaking auxiliaries or also as additives for mineral building materials, for example concrete or mortar compositions.

Examples:

The present invention will now be described with reference to the following non-binding examples.

Glossary:

- Dispersion 1: Aqueous, hydroxy-functional secondary polyacrylate dispersion,  
5 ca. 41 weight-% solids in dispersing agent water/Dowanol® PnB (propylene glycol-n-butyl ether) having a ratio of ca. 54/3,4.
- Isocyanate 1: Hydrophilic aliphatic polyisocyanate based on hexamethylene diisocyanate with an  
NCO content of ca. 20,7% to 21,7% and a monomeric isocyanate content of <  
0,5%. Used as a 70% (by weight) formulation in MPA (1-methoxy-2-propanol) or in  
10 Butoxyl® (3-methoxy-1-butyl acetate) as specified in the examples.
- Fragrant 1: Masquodor® CS 669120 containing amyl cinnamic aldehyde, citronellol,  
benzaldehyde, geraniol and terpineol
- Fragrant 2: Masquodor® CIT 669220 containing terpineol, myrcene, pinene and  
farnesol
- 15 Fragrant 3: Plastodor® CNF 661398 containing benzyl alcohol, cinnamic aldehyde,  
limonene and eugenol

Clear formulations:

- Clear coating formulations were prepared with 61,7 parts by weight of dispersion 1, 1,6 parts by  
weight of a non-ionic defoaming wetting agent, 0,1 parts by weight of a flow and leveling additive,  
20 20 parts by weight of water, 0,4 parts by weight of a rheology modifier and 19 parts by weight of  
isocyanate 1 in MPA or Butoxyl®, respectively. Depending on the example, to the isocyanate 1 were  
also added 0,2 g of fragrances 1, 2 or 3. The NCO/OH ration of the formulations (discounting  
fragrances) was 1,5, the solids content 40 weight-% and the OH group content 3%.

Testing conditions:

- 25 12 to 15 grams of each formulation were poured into a plastic container and immediately covered.  
After one and two hours the odor was evaluated: an experienced technician smelled the samples and  
graded the discernable odor of the organic solvent (MPA or Butoxyl®) on a scale of 0 to 5. A score  
of 0 means that the solvent odor has not been masked at all and a score of 5 means that the solvent

odor has been totally masked. It has been found to be advisable to smell coffee between individual evaluations.

Furthermore, the formulations were coated on plexiglass panels with a wet coating thickness of 200 microns and aged at room temperature. Herein fresh preparations of the isocyanate 1 with the  
 5 respective fragrances and preparations which had been aged for one month at room temperature were used in order to assess any influence of the fragrances on storage stability of the isocyanate. The appearance of the coating film was found to be satisfactory in all tests.

Haze-gloss was determined according to DIN 67530.

Results:

	Odor grade	Haze Gloss 20°/60°	Haze Gloss 20°/60° (aged Isocyanate 1)
Isocyanate 1 (70% in MPA)	0	9 84/90	- -
Isocyanate 1 (70% in MPA + Fragrant 1)	1	9 84/90	9 84/89
Isocyanate 1 (70% in MPA + Fragrant 2)	2	9 84/90	8 84/90
Isocyanate 1 (70% in MPA + Fragrant 3)	1	9 84/90	7 84/90
Isocyanate 1 (70% in Butoxyl®)	0	3 85/90	- -
Isocyanate 1 (70% in Butoxyl® + Fragrant 1)	1	3 85/90	3 85/90
Isocyanate 1 (70% in Butoxyl® + Fragrant 2)	1	2 85/90	3 85/90
Isocyanate 1 (70% in Butoxyl® + Fragrant 3)	3	2 85/90	3 84/90

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The tests show that the storage stability of the isocyanate is not affected. There are practically no changes in gloss and haze values between the aged and the freshly prepared mixtures of the isocyanate and the fragrances.

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Claims:

1. An aqueous composition comprising a water-emulsifiable polyisocyanate (A),  
  
the water-emulsifiable polyisocyanate (A) being a reaction product of a polyisocyanate (B) with a compound (C) which contains at least one sulfonic acid group or its anion, and at least one  
5 isocyanate-reactive group,  
  
characterized in that the composition further comprises a fragrant (D1) with at least one hydroxyl and/or aldehyde group.
2. The composition according to claim 1, further comprising propylene glycol-n-butyl ether and/or 3-methoxy-1-butyl acetate as an organic co-solvent.
- 10 3. The composition according to claim 1, wherein the fragrant (D1) is selected from the group consisting of benzaldehyde, benzyl alcohol, neral, citronellal, citronellol, farnesol, decanal, dihydrolinalool, dihydromyrcenol, dimethylphenylcarbinol, eucalyptol, geraniol, hydroxycitronellal, linalool, linalool oxide, methylnonylacetaldehyde, myrcenol, nerol, phenylethyl alcohol, alpha-terpinol, beta-terpinol, alpha-amylcinnamaldehyde, amyl salicylate, cinnamyl alcohol, cinnamyl  
15 aldehyde, ethylvanillin, eugenol, iso-eugenol, piperonal, lilial, nerolidol, patchouli alcohol, phenylhexanol, triethyl citrate, vanillin, dimethoxybenzaldehyde, hexylcinnamaldehyde and 3-and 4-(4-hydroxy-4-methyl-pentyl) cyclohexene-1-carboxaldehyde.
4. The composition according to claim 1, wherein the fragrant (D1) is present in an amount of  $\geq 0,1$  weight-% to  $\leq 3$  weight-%, based on the total amount of water-emulsifiable polyisocyanate (A).
- 20 5. The composition according to claim 1, wherein the combined amount of sulfonic acid groups and anions of sulfonic acid groups is  $\geq 0,03$  mol/kg to  $\leq 3$  mol/kg of water-emulsifiable polyisocyanate (A).
6. The composition according to claim 1, wherein the compound (C) containing at least one sulfonic acid group or its anion and at least one isocyanate-reactive group is a hydroxysulfonic acid, an  
25 aminosulfonic acid or a hemiester of sulfuric acid with a hydroxyl group or a primary or secondary amino group.
7. The composition according to claim 6, wherein the compound (C) containing at least one sulfonic acid group or its anion and at least one isocyanate-reactive group is 2-(cyclohexylamino)-ethanesulfonic acid and/or 3-(cyclohexylamino)-propanesulfonic acid and/or anions or zwitterions of  
30 the aforementioned sulfonic acids.

8. The composition according to claim 1, wherein the water-emulsifiable polyisocyanate (A) further comprises alkylene oxide units.
9. Use of a composition according to one or more of claims 1 to 8 as an adhesive, a coating or an impregnating material.
- 5 10. A substrate coated with a composition according to one or more of claims 1 to 8.

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2012/057020

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G18/00 C08G18/08 C08G18/28 C08G18/70  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/034162 A1 (LAAS HANS-JOSEF [DE] ET AL) 19 February 2004 (2004-02-19) cited in the application paragraph [0001] example 4	1-10
A	----- US 5 583 176 A (HAEBERLE KARL [DE]) 10 December 1996 (1996-12-10) cited in the application column 1, lines 4-21 examples 1-6 -----	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

7 September 2012

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/057020

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2004034162	A1	19-02-2004	AT 272660 T 15-08-2004
		AU 6899301 A 26-11-2001	
		BR 0110821 A 11-02-2003	
		CA 2408723 A1 12-11-2002	
		CN 1429240 A 09-07-2003	
		CZ 20023754 A3 12-02-2003	
		DE 10024624 A1 22-11-2001	
		EP 1287052 A1 05-03-2003	
		ES 2225571 T3 16-03-2005	
		HK 1057221 A1 07-10-2005	
		HU 0301889 A2 28-08-2003	
		JP 4806511 B2 02-11-2011	
		JP 2003533566 A 11-11-2003	
		MX PA02011372 A 06-06-2003	
		PL 358429 A1 09-08-2004	
		PT 1287052 E 31-12-2004	
		SK 16282002 A3 02-05-2003	
		TR 200402375 T4 21-12-2004	
		US 2004034162 A1 19-02-2004	
		WO 0188006 A1 22-11-2001	
US 5583176	A	10-12-1996	AT 174357 T 15-12-1998
		CA 2158621 A1 24-03-1996	
		DE 4433929 A1 28-03-1996	
		EP 0703255 A1 27-03-1996	
		US 5583176 A 10-12-1996	