



(51) International Patent Classification:

C09D 175/04 (2006.01) C08G 18/24 (2006.01)

C08G 18/79 (2006.01) C08G 18/22 (2006.01)

C08G 18/62 (2006.01) C08G 18/02 (2006.01)

C08G 18/18 (2006.01)

(21) International Application Number:

PCT/EP2018/084083

(22) International Filing Date:

10 December 2018 (10.12.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

17208340.4 19 December 2017 (19.12.2017) EP

(71) Applicant: BASF SE [DE/DE]; Carl-Bosch-Strasse 38, 67056 Ludwigshafen am Rhein (DE).

(72) Inventors: LUCAS, Frederic; Carl-Bosch-Strasse 38, 67056 Ludwigshafen (DE). PANCHENKO, Alexander; Carl-Bosch-Strasse 38, 67056 Ludwigshafen (DE). SCHAEFER, Harald; Carl-Bosch-Strasse 38, 67056 Ludwigshafen (DE).

(74) Agent: BASF IP ASSOCIATION; BASF SE, G-FLP - C006, 67056 Ludwigshafen (DE).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

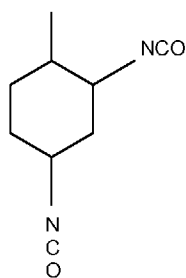
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

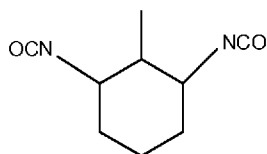
Published:

— with international search report (Art. 21(3))

(54) Title: COATING COMPOSITION COMPRISING THE ISOCYANURATE OF A CYCLOALIPHATIC DIISOCYANATE



(I)



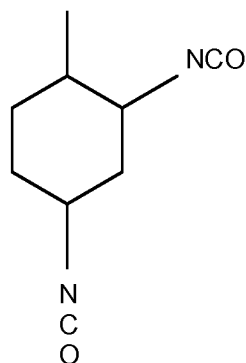
(II)

(57) Abstract: Coating composition comprising a trimerization product of diisocyanates, wherein at least 50 % by weight of the diisocyanates are a cycloaliphatic diisocyanate selected from a diisocyanate of formula (I), a diisocyanate of formula (II) or a mixture thereof.

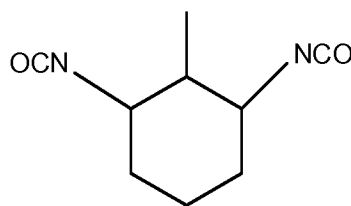


Coating composition comprising the isocyanurate of a cycloaliphatic diisocyanate

The present invention relates to a coating composition comprising a trimerization product of diisocyanates, wherein at least 50 % by weight of the diisocyanates are a cycloaliphatic diisocyanate selected from a diisocyanate of formula I



10 a diisocyanate of formula II



or a mixture thereof.

15

Coating compositions comprising compounds with isocyanate groups and compounds that are reactive with isocyanate groups, such as hydroxy or amino compounds are well-known.

20

Compounds with two isocyanate groups - hereinafter referred to as diisocyanates - often have a volatility which is not low enough to be useful in coating applications. Therefore, low molecular diisocyanates may be reacted to compounds of higher molecular weight which have less volatility, such as dimers or trimers of the diisocyanate. A suitable dimer of diisocyanates are uretdi-ones, a suitable trimer of diisocyanates are isocyanurates. The higher molecular weight is advantageous in respect to toxicology and functionality as well.

25

Due to the high reactivity of the isocyanate group, coating compositions usually are two-component coating compositions. A first component comprises the compounds with isocyanate groups and the second component comprises the compounds that are reactive with isocyanate, such as compounds with hydroxy or amino groups. After mixing the two components the isocyanate groups react with the hydroxy or amino groups and form the polyurethane or polyurea coating. It

30

is desired that the obtained mixture remains usable when mixed, at least for a certain time. The time during which the mixture remains usable is known as pot life.

EP-A 2289963 discloses two component coating compositions comprising isocyanurates of isophorone diisocyanate.

With isocyanurates used so far, the pot life often is too short.

EP-A 0761670 discloses polycyclic imino-oxa-diazindiones obtained from linear or cyclic diisocyanates and their use in coating compositions. The cyclic diisocyanates include 1,3-diisocyanato-2-methylcyclohexane, 1,3-diisocyanato-4-methylcyclohexane and mixtures thereof.

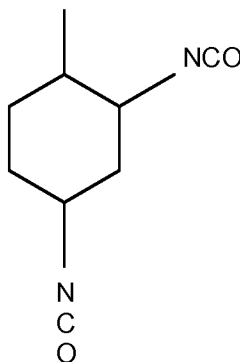
An improved process for the preparation of cyclic diisocyanates including 1,3-diisocyanato-2-methylcyclohexane, 1,3-diisocyanato-4-methylcyclohexane and mixtures thereof is known from WO 17/013154. An improved process for the preparation of isocyanurates of cyclic diisocyanates is subject of the EP patent application with application number 16200079.8 (INV 150011).

It was an object of this invention to provide two component coating compositions of isocyanate compounds and compounds reactive with isocyanate that have an extended pot life and result in coatings with improved or at least satisfying properties.

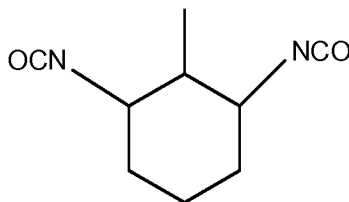
Accordingly, the coating composition described above has been found.

To the trimerization product:

The coating composition comprises a trimerization product of diisocyanates, wherein at least 50 % by weight of the diisocyanates are a cycloaliphatic diisocyanate selected from a diisocyanate of formula I



a diisocyanate of formula II



or a mixture thereof

Preferably, the cycloaliphatic diisocyanate is a mixture of the diisocyanates of formula I and II. More preferably, the cycloaliphatic diisocyanate is a mixture of 50 to 95 % by weight of the diisocyanate of formula I and 5 to 50 % by weight of the diisocyanate of formula II.

In a most preferred embodiment of the invention, the cycloaliphatic diisocyanate is a mixture of 70 to 90 % by weight of the diisocyanate of formula I and 10 to 30 % by weight of the diisocyanate of formula II. The weight percent relate to the total weight of the diisocyanates of formula I and II.

The two isocyanate groups in formula I and II may be in cis or trans position to the cyclohexane ring. Cis position means that both isocyanate groups are on the same side of the cyclohexane ring. Trans position means that the two isocyanate groups are on opposite sides of the cyclohexane ring.

Preferably, the isocyanate groups are in trans position to the cyclohexane ring in more than 70 mol% of the cycloaliphatic diisocyanate, notably in more than 90 mol% of the cycloaliphatic diisocyanate.

The cycloaliphatic diisocyanate and the synthesis thereof are known. The synthesis is described, for example, in WO 17/013154. Starting material are the corresponding toluene diamines which are hydrogenated to obtain 1,3-diamino-2-methylcyclohexane, 1,3-diamine-4-methylcyclohexane or mixtures thereof. The amino groups are transferred into isocyanate groups by reacting with phosgene before or after the hydrogenation, preferably thereafter.

The proportion of isocyanate groups that are in trans or cis position depends from the diamino-methyl cyclohexane used as starting material. If the diamino-methyl cyclohexane comprises too much amino groups which are in cis transition, the corresponding isomers of the diamino-methyl cyclohexane may be separated, for example according to the process disclosed in WO 2016/083210 and the trans enriched diamino-methyl cyclohexane may be used for the further synthesis of the cycloaliphatic diisocyanate of formula I and II.

The trimerization product of the diisocyanates is preferably a mixture comprising an isocyanurate formed from three diisocyanates and compounds of higher molecular weight resulting from further trimerization reactions of the isocyanate groups of the isocyanurate. Such compounds with higher molecular weight are, for example, the trimerization product composed of five diisocyanates and comprising two isocyanurate ring systems or the trimerization product composed of seven diisocyanates and comprising three isocyanurate ring systems. The synthesis of such trimerization products, respectively isocyanurates, is well known. The trimerization product is obtained by cyclo-trimerization of the diisocyanates in the presence of a trimerization catalyst. A preferred trimerization process for cycloaliphatic diisocyanates is disclosed in EP patent application with application number 16200079.8 (INV 150011).

Preferably, the trimerization products consists to at least 40 % by weight, notably to at least 50 % by weight of the isocyanurate formed from three diisocyanates.

The trimerization product may be formed from the cycloaliphatic diisocyanates of formula I and II, only. Alternatively, a mixture of cycloaliphatic diisocyanates of formula I and II and other diisocyanates may be used as starting materials for the trimerization. In this case, the obtained trimer comprises the cycloaliphatic diisocyanates of formula I and II in an amount corresponding to the composition of the mixture.

Preferably, the trimerization product is a trimerization product of diisocyanates, wherein at least 70 % by weight, notably to at least 95 % by weight of the diisocyanates are a cycloaliphatic diisocyanate selected from a diisocyanate of formula I, of formula II or mixtures thereof.

In a particularly preferred embodiment the trimerization product is a trimerization product of diisocyanates, wherein 100% by weight of the diisocyanates are a cycloaliphatic diisocyanate selected from a diisocyanate of formula I, of formula II or mixtures thereof.

To the coating composition

The coating composition comprises the above trimer and compounds that react with isocyanate groups.

Preferably, the coating composition comprises the trimer, further compounds with at least one isocyanate group and compounds that react with isocyanate groups.

To further compound with at least one isocyanate group

Further compounds with at least one isocyanate group are compounds with one isocyanate group – hereinafter referred to as monoisocyanate, compounds with two isocyanate groups – hereinafter referred to as diisocyanates and compounds with at least three isocyanate groups – hereinafter referred to as polyisocyanates.

Monoisocyanates are used to limit the molecular weight of the obtained polymer. Hence, monoisocyanates are used only optionally and – if used – they are used in low amounts, only.

- 5 Preferred diisocyanates are diisocyanates of formula $X(NCO)_2$, where X is an aliphatic hydrocarbon radical having 4 to 12 carbon atoms, a cycloaliphatic or aromatic hydrocarbon radical having 6 to 15 carbon atoms, or an araliphatic hydrocarbon radical having 7 to 15 carbon atoms. Examples of such diisocyanates are tetramethylene diisocyanate, hexamethylene diisocyanate (HDI), dodecamethylene diisocyanate, 1,4-diisocyanatocyclohexane, 1-isocyanato-3,5,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI), 2,2-bis(4-isocyanatocyclohexyl)-propane, trimethylhexane diisocyanate, 1,4-diisocyanatobenzene, 2,4-diisocyanatotoluene, 2,6-diisocyanatotoluene (TDI), 4,4'-diisocyanato-diphenylmethane, 2,4'-diisocyanatodiphenylmethane (MDI), p-xylylene diisocyanate, tetramethylxylylene diisocyanate (TMXDI), the isomers of bis(4-isocyanatocyclohexyl)methane (HMDI), pentamethylene diisocyanate (PDI) such as any mixtures of these compounds.

Diisocyanates include dimers of the compounds listed above, notably uretdiones or allophanates.

- 20 Polyisocyanates are, in particular, compounds with three isocyanate groups such as isocyanurates obtained by trimerization of diisocyanates or biurets obtained from diisocyanates.

In a preferred embodiment of the invention, the coating composition comprises the above trimerization product of the diisocyanates and, in addition, further compounds with at least one isocyanate group.

25

In a preferred embodiment, the coating composition comprises

- 10 to 90 % by weight of the above trimerization product,
10 to 90 % by weight of further polyisocyanates and
30 0 to 50% by weight of further compounds with one or two isocyanate group

based on the total weight of all compounds with at least one isocyanate group.

- In a particularly preferred embodiment, the coating composition comprises

35

10 to 50 % by weight of the above trimerization product,
50 to 90 % by weight of further polyisocyanate and
0 to 20 % by weight of further compounds with one or two isocyanate group

- 40 based on the total weight of all compounds with at least one isocyanate group.

Preferably, the further polyisocyanate is an aliphatic polyisocyanate. More preferably the further polyisocyanate is an aliphatic isocyanurate.

- 5 Most preferably, the further polyisocyanate is selected from the isocyanurate of HDI, the isocyanurate of IPDI, the isocyanurate of PDI and mixtures thereof.

In a preferred embodiment, at least 60 % by weight of all compounds with at least one isocyanate group are the above trimerization product and further polyisocyanates.

- 10 More preferably, at least 90%, notably at least 95% by weight of all compounds with at least one isocyanate group are the above trimerization product and further polyisocyanates.

To the compounds that react with isocyanate groups

- 15 Compounds that react with isocyanate groups are, in particular, compounds with at least one functional group selected from hydroxy groups, primary or secondary amino groups or mercaptane groups.

- 20 Compounds with only one functional group that react with isocyanate are used to limit the molecular weight of the obtained polymer. Hence, such compounds are used only optionally and – if used- they are used in low amounts, only.

- 25 Preferably, compounds that react with isocyanate groups are selected from compounds with at least two hydroxy groups and compounds with at least two primary or secondary amino groups.

In a preferred embodiment of the invention, at least 50 mol%, in particular at least 80 mol %, most preferably at least 95 mol % of all compounds that react with isocyanates are compounds with at least two hydroxy groups. The obtained polymer is a polyurethane.

- 30 Compounds with at least two hydroxy groups are preferably polyetherpolyols, polyesterpolyols or polymers with at least two hydroxy groups which are obtainable by radical polymerization of ethylenically unsaturated compounds herein referred to as monomers.

- 35 Preferred polyesterpolyols have two to eight, preferably two to five hydroxy groups, more preferably two or three, in particular two hydroxy groups and are obtainable by reacting polyols, which include notably diols, with polycarboxylic acids which include notably dicarboxylic acids.

- 40 The polycarboxylic acids can be aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic and can if appropriate be substituted, by halogen atoms for example, and/or unsaturated. Examples thereof include the following: suberic acid, azelaic acid, phthalic acid, isophthalic acid, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic acid, hexahydrophthalic an-

hydride, tetrachlorophthalic anhydride, endomethylenetetrahydrophthalic anhydride, glutaric anhydride, maleic acid, maleic anhydride, fumaric acid, and dimeric fatty acids. Preferred dicarboxylic acids are those of the formula $\text{HOOC}-(\text{CH}_2)_y-\text{COOH}$, where y is a number from 1 to 20, preferably an even number from 2 to 20, examples being succinic acid, adipic acid, sebacic acid, and dodecanedicarboxylic acid.

Examples of suitable polyols include ethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,3-diol, butene-1,4-diol, pentane-1,5-diol, neopentyl glycol, bis(hydroxymethyl)cyclohexanes such as 1,4-bis(hydroxymethyl)cyclohexane, 2-methylpropane-1,3-diol, methylpentanediols, and diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, dipropylene glycol, polypropylene glycol, and dibutylene glycol and polybutylene glycols. Preferred polyols are those of the formula $\text{HO}-(\text{CH}_2)_x-\text{OH}$, where x is a number from 1 to 20, preferably an even number from 2 to 20. Examples of such include ethylene glycol, butane-1,4-diol, hexane-1,6-diol, octane-1,8-diol, and dodecane-1,12-diol. Preference is also given to neopentyl glycol.

The number-average molecular weight M_n of the polyesterpolyol is preferably at least 500 g/mol, more preferably at least 700 g/mol. The upper limit of the molecular weight M_n is preferably 30 000 g/mol, more preferably 10 000 g/mol, very preferably 4000 g/mol. In a preferred embodiment, the polyesterpolyol has a molecular weight M_n being from 500 to 4000, more particularly from 700 to 2000 g/mol. The polydispersity M_w/M_n is preferably 1.1 – 50, more preferably less than or equal to 5, more particularly less than 3.5.

Preferred polyetherpolyols have two to eight hydroxy groups, preferably two to five hydroxy groups, most preferably two hydroxy groups and are obtainable in particular by polymerizing ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, styrene oxide or epichlorohydrin with itself, in the presence of a catalyst, which is, for example, BF_3 and a starter component containing reactive hydrogen atoms, such as alcohols or amines, examples being water, ethylene glycol, propane-1,2-diol, propane-1,3-diol, 1,2-bis(4-hydroxydiphenyl)propane, and aniline. A preferred polyetherpolyol is polytetrahydrofuran with a molecular weight of from 240 to 5000, and notably of from 500 to 4500.

A preferred polymer with at least two hydroxy groups is a polymer obtained by polymerization of acrylic or methacrylic compounds (herein referred to as (meth)acrylics) and optionally further monomers as e.g. styrene, whereby at least 50 mol %, more preferably at least 80 mol % of all monomers are (meth)acrylics. Such a polymer is hereinafter referred to as poly(meth)acrylate – polyol.

Poly(meth)acrylate – polyols are usually copolymers of (meth)acrylic esters, examples being C_1 – C_{20} alkyl (meth)acrylates, with hydroxyalkyl (meth)acrylates, examples being the mono(meth)acrylic esters of 1,2-propanediol, ethylene glycol, 1,3-propanediol, 1,4-butanediol or 1,6-hexanediol and optionally other monomers such as vinylaromatic monomers, in particular styrene, vinyl ester, in particular vinyl acetate, ethylenically unsaturated nitriles, aliphatic hydrocarbons having 2 to 8 C atoms and 1 or 2 double bonds, vinyl ethers, aliphatic

hydrocarbons having 2 to 8 C atoms and 1 or 2 double bonds and α,β -unsaturated carboxylic acids and their anhydrides which includes, for example (meth)acrylic acid, maleic acid and maleic anhydride.

- 5 The poly(meth)acrylate – polyols preferably have a molecular weight M_n (number average), as determinable by gel permeation chromatography, of 500 to 50 000 D, more particularly 500 to 10 000 D or 500 to 5000 D. In one preferred embodiment, they have a molecular weight M_n of 800-2000 D. Such poly(meth)acrylate polyols are usually used for coating materials with low solids contents. Preferred poly(meth)acrylate – polyols have OH numbers, measured according to DIN 53240-2:2007-11, of 15-250 mg KOH/g resin solids, preferably 60-180 mg KOH/g, more preferably 80-160 mg KOH/g. The poly(meth)acrylate – polyols may additionally have an acid number to BS EN ISO 3682/BS 6782-3 of less than 100 mg KOH/g, preferably less than 30, and more preferably less than 20 mg KOH/g.
- 10
- 15 Preferably, the coating composition comprises a poly(meth)acrylate - polyol as compound that reacts with isocyanate.
In a particularly preferred embodiment of the invention, at least 50 % by weight, more preferably at least 70 % by weight and most preferably at least 90% by weight of all compounds that react with isocyanate are poly(meth)acrylates - polyols.
- 20
- To the coating composition
- The coating composition comprises compounds with isocyanate groups and compound that are reactive with isocyanate preferably in an amount that the molar ratio of isocyanate groups to isocyanate-reactive groups is of from 0.5:1 to 2:1, preferably 0.7:1 to 1.3:1, more preferably 0.8:1 to 1.2:1, and especially 0.9:1 to 1.1:1.
- 25
- The coating composition preferably is a two-component coating composition with a first component comprising the trimer and any further compounds with isocyanate groups and the second component comprises all compounds that are reactive with isocyanate groups. Both components are usually mixed short before the application thereof; the compounds react and the coating which is preferably a polyurethane coating is formed.
- 30
- The coating composition may comprise further compounds besides isocyanate compounds and isocyanate-reactive compounds. Such further compounds are, in particular, solvents, catalysts, in particular, catalysts for the urethanization and additives such as UV stabilizers, thickeners, thixotropic agents, surface-active agents, viscosity modifiers, plasticizers or chelating agents, fillers, dyes and pigments, drying agents, antistatic agents, antioxidants or flame retardants.
- 35
- 40 In case of a two-component coating composition the further compounds may form part of either of both components or of both components.

The coating compositions preferably is a liquid coating composition. As some of the compounds may be solid, a solvent is required. In particular, the above trimerization product and other polyisocyanates are usually solid at room temperature. Preferably, they are solved in a solvent. The solvent may be a reactive solvent, such as a diisocyanate or a non-reactive solvent such as usual organic solvents. Water is preferably not used as solvent. Hence, the coating composition comprises no water or water in small, residual amounts, for example in amounts of preferably less than 2 % by weight, more preferably less than 0.5 % by weight and most preferably less than 0.05 % by weight based on the total weight of the coating composition. The organic solvent preferably is an aprotic solvent or mixture of aprotic solvents. The solvent should not comprise any group that is reactive with isocyanate.

Suitable organic solvents, are notably aromatic compounds including alkylated benzenes and naphthalenes, (cyclo)aliphatic hydrocarbons and mixtures thereof, chlorinated hydrocarbons, ketones, esters, alkoxyated alkyl alkanoates, ethers, and mixtures thereof.

Preferred solvents are n-butyl acetate, ethyl acetate, 1-methoxyprop-2-yl acetate, 2-methoxyethyl acetate, xylene and Solvesso® 100.

Preferably, the coating composition further comprises an urethanization catalyst or mixture of urethanization catalysts. Urethanization catalysts are compounds with the capacity to accelerate the reaction of isocyanate groups with groups that are reactive toward isocyanate. The urethanization catalyst is preferably a Lewis base and preferably has a pKa of more than 8, determined in water. In one preferred embodiment of the present invention, the Lewis base is an organic amine. The urethanization catalysts may, for example, be tertiary aliphatic, cycloaliphatic, aromatic amines, amidines, guanidines or ionic liquids containing amine groups. The urethanization catalyst may as well be a metal based Lewis acid derived from e.g. tin, zinc, bismuth, titanium or zirconium.

The urethanization catalyst is preferably used in amounts of 0.1 to 2 parts by weight per 100 parts by weight of compounds with at least one hydroxy group.

UV stabilizers are, in particular, UV absorbers and radical scavengers (especially HALS compounds, hindered amine light stabilizers).

To the application as coating

The coating composition of this invention is preferably used for the preparation of coatings. In case of the two-components coating composition, the two components are preferably mixed short before the application.

The coating composition may be applied to substrates of all kind.

The coating composition is suitable for coating substrates such as wood, wood veneer, paper, cardboard, paperboard, textile, film, leather, nonwoven, plastics surfaces, glass, ceramic, mineral building materials, such as molded cement blocks and fiber-cement slabs, or metals, which in each case may optionally have been precoated or pretreated. Preference is given to wood, metals and plastics, which may optionally have been precoated or pretreated. Particularly preferred are metals and plastics.

The coating composition is suitable as or in interior or exterior coatings, i.e., in those applications where there is exposure to daylight, coatings on (large) vehicles and aircraft, and industrial applications, railways, utility vehicles in agriculture and construction, especially known as ACE (agricultural, construction and earthmoving equipment), wind turbines, bridges, power masts, tanks, containers, pipelines, power stations, chemical plants, ships, cranes, halls, roofs, furniture, windows, doors, wood flooring, paper, board, for floor coverings, such as in parking levels or in hospitals and in particular in automotive paints as refinish. Preferred are refinish, plastics, and industrial applications, ACE for example.

In particular, the coating composition of the invention is used in coatings applications as clearcoat, basecoat, topcoat, primer or surfacer materials, especially as clearcoat or topcoat materials.

The substrates may be coated by typical methods known to the skilled person, for example by spraying, troweling, knife coating, brushing, rolling, roller coating, pouring, laminating, injection-back molding or coextruding. The thickness of a film of this kind for curing may be from 0.1 μm up to several mm, preferably from 1 to 2000 μm , more preferably 5 to 200 μm , very preferably from 5 to 60 μm .

The applied coating compositions may be cured by any method known to the skilled person. Preferably curing occurs at room temperature or by heating to elevated temperatures, notably to temperatures of up to 80°C. Curing may also take place with and/or be assisted by infrared radiation.

The coating compositions are especially suitable for applications requiring particularly high application reliability, exterior weathering resistance, optical qualities, solvent resistance, chemical resistance and water resistance.

The coating composition of the invention has an extended pot life. After mixing the two components of the two-component coating composition the obtained mixture usable for a longer time. The obtained coatings have high performance and have very good mechanical properties and chemical resistance.

Examples:

Compounds used

5 Polyisocyanat A:

Isocyanurate of hexamethylene-diisocyanate (HDI-Isocyanurate), 2800 mPa*s, 22.0% by weight of NCO, Basonat® HI 100 of BASF

Polyisocyanat B:

- 10 Isocyanurate of isophorone-diisocyanate (IPDI-Isocyanurate), solved in in Solvesso 100, 11.7 % by weight of NCO, solid content 70% by weight, Vestanat 1890® of Evonik SE.

Polyisocyanat C:

A mixture of

- 15 50% by weight of the isocyanurate of a mixture of compound of formula I and II (produced according to EP application number 16200079. and
50% by weight of IPDI – isocyanurate,
solved in Solvesso 100, solid content 70 %, 12.3% by weight NCO.

20 Polyacrylat-polyol 1:

Polyacrylat with OH number of 145 mg KOH/g, solid content 80% by weight in butyl acetate, glass transition point -7°C, Joncryl® 507 of BASF SE

Polyacrylat-polyol 2:

- 25 Polyacrylat with OH number of 140 mg KOH/g, solid content 80% by weight in xylene, glass transition temperature -4°C; Joncryl® 510 of BASF

DABCO TMR®:

- 30 N-(2-hydroxypropyl)-N,N,N-trimethylammonium 2-ethylhexanoate, 75% in ethylene glycol, product of Air Products

DBTL

Dibutyltin dilaurate, catalyst, Aldrich, 1% in solution

35 Borch® Kat 22

Zinc bis(2-ethylhexanoate), 100%, OMG Borchers

Preparation of the coatings

- 40 The compounds listed in the Table were mixed. Further butylacetate has been added in amounts listed in Table 1 so that all mixtures have the same viscosity.
Immediately thereafter the coating compositions were coated using a four-way bar coater (doctor blade) in a dry film thickness of 35-45 µm; the wet film thickness was 150 µm.

The obtained coatings were cured at $23 \pm 2^\circ\text{C}$ and $50 \pm 10\%$ humidity for determination of the pendulum hardness.

- 5 For other testings, the obtained coatings were first kept at room temperature for 10-15 minutes. Thereafter they were kept at 60°C for 30 minutes. The curing was followed by conditioning at $23 \pm 2^\circ\text{C}$ and $50 \pm 10\%$ humidity and for 24 hours unless explicitly stated otherwise.

Test methods:

10

Viscosities

Viscosities are reported at 23°C in accordance with DIN EN ISO 3219/A.3 in a cone/plate system with a shear rate of 1000 s^{-1} .

15 Gel time

- The liquid coating was prepared as described above and was directly after its preparation introduced into a test tube (20 mm x 180 mm) with a copper pad (about 5 mm x 5 mm) attached adhesively at the bottom end. The fill level of the test tube was at least 60%. The test tube was placed into a slot in the gel time apparatus. Here, a contact was closed between copper pad and gel time apparatus. A metal spoke with a bent tip was clamped into the spoke holder at a length of 22 cm. The spoke holder was then inserted into the apparatus. This caused the spoke to be immersed in the liquid paint. The opening of the test tube was closed with a perforated lid. The spoke was guided through the hole in the lid. When the apparatus was started up, a counter was initiated. Furthermore, the assembly moved the spoke in the sample up and down until the sample became solid or gelled. When the test tube was subsequently lifted, the contact of the copper pad was lost, and the counter of the apparatus was halted automatically. Measurement took place at $23 \pm 2^\circ\text{C}$ and $50 \pm 10\%$ humidity.

- 30 The gel time listed in the table is the time when the contact of the copper pad was lost. A long gel time corresponds to a long pot life.

Dust dry time

- 35 To determine the dust dry time, the coating was applied to a glass plate at room temperature and the paint surface was contacted with a cotton pad at intervals of time. The coating is considered dust dry when cotton no longer remains sticking to the surface. Measurement took place at ambient temperature. The time until the cotton did not stick any more to the surface is listed in table 2.

Pendulum hardness

- 40 The pendulum hardness was determined by the method of Koenig on glass plates (DIN EN ISO 1522).

Cross-cut

The cross-cut was determined in accordance with DIN EN ISO 2409 on a Bonder panel.

The obtained coatings were first kept at room temperature for 10-15 minutes. Thereafter they were kept at 60°C for 30 minutes. The curing was followed by conditioning at $23 \pm 2^\circ\text{C}$ and $50 \pm 10\%$ humidity for one day (1d) or seven days (7d). The adhesion of the coating to the panel was judged pursuant to a scale of 0 to 5 with 0 standing for "no detachment of the coating layer observed" and 5 standing for "full detachment".

Gloss

The gloss of the paint was determined by means of a Mikro TRI-Gloss instrument at an angle of 20 and 60° and at a temperature of 60°C.

Chemical resistance

For the determination of the chemical resistance a coated, deep-drawn metal panel was thermally conditioned at 130°C, respectively at 60°C for 30 minutes and for 7 d (examples E1, C1) respectively 5 d (examples E2, C2) at $23 \pm 2^\circ\text{C}$ and $50 \pm 10\%$ humidity. The panel has been treated with sulfuric acid (1% strength; 25 µl).

The panel was then placed into the gradient oven (from BYK Gardner) and thermally conditioned at 30-75°C for 30 minutes. After the end of this operation, the panel was cleaned to remove the sulfuric acid, using fully demineralized water. Then, the panel was washed off thoroughly but gently using cold water, and the remaining drops of water were removed using a soft paper towel. After 24 hours of conditioning at $23 \pm 2^\circ\text{C}$ and $50 \pm 10\%$ humidity, evaluation took place. The temperature in the table is the temperature at which the first attack on the coating is perceptible under artificial light with the eyes.

Table 1: coating compositions in gram (g)

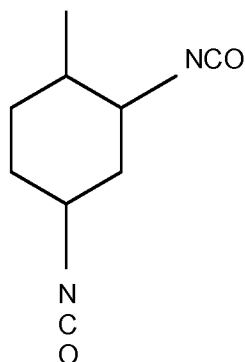
	Example 1 (E1)		Comparison (C1)		Example 2 (E2)		Comparison example 2 (C2)	
	Total weight	Sol- ids (with- out sol- vent)	Total weight	Sol- ids (with- out sol- vent)	Total weight	Sol- ids (with- out sol- vent)	Total weight	Sol- ids (with- out sol- vent)
Polyacrylatole 2	60.0	48.0	60.0	48.0				
Polyacrylatole 1					60.0	48.0	60.0	48.0
Polyisocyanate A	16.1	16.1	16.1	16.1	16.0	16.0	16.0	16.0
Polyisocyanate C	12.3	8.6			12.3	8.6		
Polyisocyanate B			12.9	9.0			12.9	9.0
Butylacetate	35.00		35.00		32.70		32.20	

Table 2: results of application tests

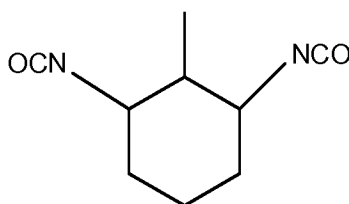
	E1	C1	E2	C2
- Dust dry time [min]	> 300	> 300	>200	>200
Pendulum hardness on glass substrate (numbers of oscillations)				
4 h	sticks	sticks	sticks	sticks
1 d	13	15	8	12
2 d	38	36	39	38
3 d	50	51	57	54
6 d	74	79	71	71
7 d	77	84	89	93
7 d + 15 h 60 °C	97	108	116	121
Gel time (hours : minutes)	45:56	7:52	39:28	4:52
Cross cut				
Cross cut 1 d	1	1	1	2
Cross cut 7 d	2	2	5	3
Gloss 60 °C; 20°/60° [%]	85 / 95	85 / 92	92/96	92/96
Haze 60 °C 20°	21	21	18	18
Levelling on tin plate	ok	ok	ok	ok
Chemical resistance				
60 °C; 1% sulfuric acid (°C)	42	45	45	45
130 °C; 1% sulfuric acid (°C)	50	48	48	56

Claims

1. Coating composition comprising a trimerization product of diisocyanates, wherein at least 50 % by weight of the diisocyanates are a cycloaliphatic diisocyanate selected from a diisocyanate of formula I



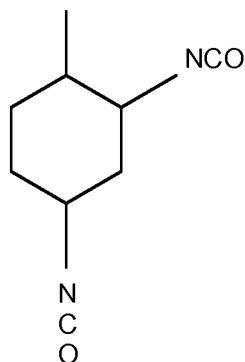
a diisocyanate of formula II



or a mixture thereof.

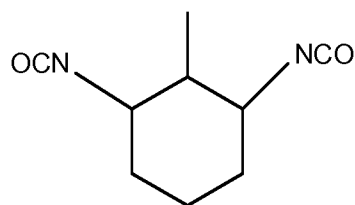
2. Coating composition according to claim 1 wherein the cycloaliphatic diisocyanate is a mixture of diisocyanates of formula I and II.
3. Coating composition according to claims 1 or 2, wherein the cycloaliphatic diisocyanate is a mixture of 50 to 95 % by weight of the diisocyanate of formula I and 5 to 50 % by weight of the diisocyanate of formula II.
4. Coating composition according to any of claims 1 to 3, wherein in more than 70 mol% of the cycloaliphatic diisocyanate the isocyanate groups are in trans position to the cyclohexane ring.
5. Coating composition according to any of claims 1 to 4, wherein at least 95 % by weight of the diisocyanates are a cycloaliphatic diisocyanate selected from a diisocyanate of formula I, of formula II or a mixture thereof.

6. Coating compositions according to any of claims 1 to 5, wherein the coating composition comprises the trimerization product, further compounds with isocyanate groups and compounds that react with isocyanate groups.
- 5 7. Coating composition according to claim 6 wherein the compounds that react with isocyanate groups are selected from compounds with at least two hydroxy groups and compounds with at least two primary or secondary amino groups.
- 10 8. Coating composition according to claim 6 or 7 wherein the coating composition comprises
- 10 to 90 % by weight of the trimerization product
10 to 90 % by weight of further compounds with at least three isocyanate groups, hereinafter referred to as polyisocyanates, and
0 to 50% by weight of further compounds with one or two isocyanate group
- 15 based on the total weight of all compounds with at least one isocyanate group.
9. Coating composition according to any of claims 1 to 8 wherein the coating composition is a two-component coating composition with a first component comprising the trimerization product and any further compounds with isocyanate groups and the second component comprises all compounds that are reactive with isocyanate groups.
- 20 10. Use of the coating composition according to any of claims 1 to 9 for the preparation of coatings.
- 25 11. Use of the coating composition according to any of claims 1 to 9 for the preparation of polyurethane coatings.
- 30 12. Trimerization product of diisocyanates, wherein at least 50 % of the diisocyanates is a cycloaliphatic diisocyanate selected from a diisocyanate of formula I



17

a diisocyanate of formula II



or a mixture thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/084083

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C09D175/04	C08G18/79
	C08G18/22	C08G18/02
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)		
C09D 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, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 966 338 A (ICI LTD) 12 August 1964 (1964-08-12) page 1, lines 9-54 page 2, lines 53-118 example 10	1-12
A	----- WO 2016/083210 A1 (BASF SE [DE]) 2 June 2016 (2016-06-02) cited in the application page 1, line 5 - page 3, line 15 page 10, line 5 - page 11, line 29 examples 1,3,4	1-12
A	----- US 2001/027243 A1 (KOHLESTRUK STEPHAN [DE] ET AL) 4 October 2001 (2001-10-04) paragraphs [0001] - [0012] paragraph [0015] -----	1-12
☐ 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		Date of mailing of the international search report
11 February 2019		21/02/2019
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Neugebauer, Ute

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2018/084083

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 966338	A	12-08-1964	NONE	

WO 2016083210	A1	02-06-2016	CN 107001237 A	01-08-2017
			EP 3224235 A1	04-10-2017
			JP 2017537095 A	14-12-2017
			KR 20170086518 A	26-07-2017
			US 2017260115 A1	14-09-2017
			WO 2016083210 A1	02-06-2016

US 2001027243	A1	04-10-2001	DE 10015890 A1	11-10-2001
			EP 1138705 A1	04-10-2001
			JP 2001323039 A	20-11-2001
			US 2001027243 A1	04-10-2001
