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(54) Title: NON-CRYSTALLISING BIS-OXAZOLIDINES

(57) Abstract: The present invention relates to non-crystallising oxazolidines as curing agents for polyisocyanates, respectively polyurethanes. These curing agents are essentially mixtures of at least one polyoxazolidine POU having at least two urethane groups and at least one polyoxazolidine POC having at least one carbonato group.

NON-CRYSTALLISING BIS-OXAZOLIDINES

Technical field

The invention relates to the field of oxazolidines curing agents for polyisocyanates, respectively polyurethanes.

Background of the invention

Oxazolidines, particularly bis-oxazolidines, are well known as curing agents for polyurethanes. Particularly useful as curing agents are bis-oxazolidines which are linked by urethane groups, disclosed for example in US 5,747,627, US 5,189,176 and GB 1 463 944.

A further class of oxazolidines are bis-oxazolidines which are linked by carbonato groups. Such bis-oxazolidines are disclosed for example in EP 0 499 188 A1.

A further class of oxazolidines are bicyclic oxazolidines which are disclosed for example in US 5,126,421, WO 96/08308 A1, WO 99/07762 A1 and GB 1 292 455.

Polyoxazolidines in general, and particularly polyoxazolidines having urethane groups, however, tend to crystallize. This is very disadvantageous in view of storage, transport and application of these compounds. There have been several approaches to solve this problem. The use of solvents show disadvantages such as impairment of mechanical properties and release of solvents (VOC: Volatile Organic Compounds). US 5,189,176 suggests a non-crystallising bisoxazolidine having two urethane groups linked together by a hexamethylene group and having a hydrocarbon substituent with 5 to 8 carbon atoms attached to the carbon located between the oxygen and nitrogen atom of the oxazolidine ring. However, this very narrow group of chemical compounds is very restrictive in the choice of suitable properties of polyoxazolidines.

Summary of the invention

Therefore, the problem to be solved by the present invention is to offer non-crystallising polyoxazolidines that provide a broad choice of properties of polyoxazolidines. This problem can be solved by a composition according to the features of claim 1.

Furthermore, these polyoxazolidines are not based on solvents and, therefore, are ecologically and economically advantageous. The most important advantage is that a broad range of existing crystallising polyoxazolidines can be modified to yield non-crystallising polyoxazolidine compositions according to the invention. This allows for the possibility to tailor the curing properties to the customers' needs.

Further aspects of the invention are subject of further main claims. Preferred embodiments are subject of the depending claims.

Detailed description of the invention

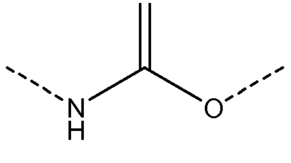
The present invention relates in a first aspect to a composition comprising:

a) at least one polyoxazolidine **POU** having at least two urethane groups and

b) at least one polyoxazolidine **POC** having at least one carbonato group.

All bold indications in this document such **POU**, **POC**, **BCO** or alike are used only for informative purposes and serve only to aid understanding and identification.

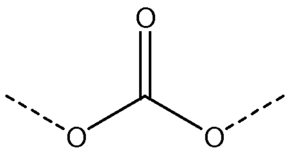
The term “urethane groups” shall mean in the present document a group of the formula (a).



(a)

Dotted lines indicate in the present document the binding site to other substituents.

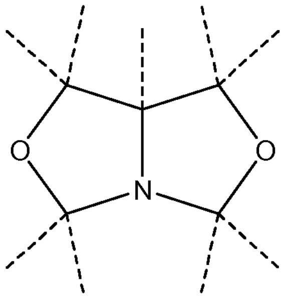
The term “carbonato group” shall mean in the present document a group of the formula (b).



(b)

The term “room temperature” shall mean in the present document a temperature of 25°C.

The term “bicyclic polyoxazolidine” shall mean in the present document a compound having two oxazolidines ring which are fused together, in other words a compound comprising the structural element of the formula (c)



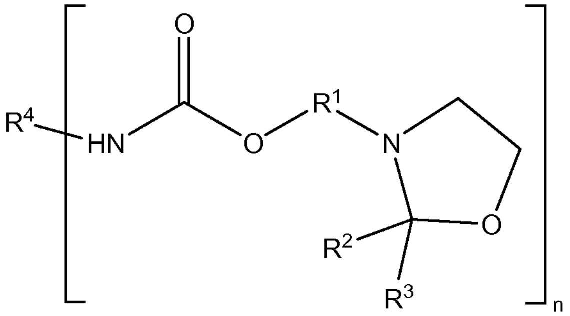
(c)

The term “consists essentially of” shall mean in the present document that, apart from the mentioned components, only minor amounts, i.e. typically less than 5 % by weight, particularly less than 1 % by weight, of other ingredients are present.

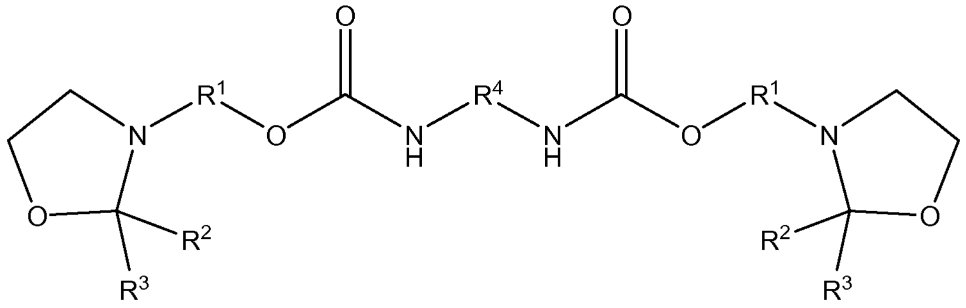
The term “polyurethane” shall mean any product of the addition reaction of polyisocyanate and polyols and/or polymercaptans and eventually water, independently whether some isocyanate groups remain or not. Particularly, the so-called polyurethane prepolymers, which are curable by humidity due to the isocyanate groups, are also regarded as polyurethanes as well as the completely cured polymer having essentially no NCO groups left.

The composition comprises at least one polyoxazolidine **POU** having at least two urethane groups.

Preferably the polyoxazolidine **POU** having at least two urethane groups has a structure according to formula (I), particularly to formula (Ia).



(I)



(Ia)

wherein

R^1 is an alkylene group with 2 to 5 carbon atoms, particularly an ethylene group;

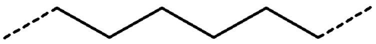
R^2 and R^3 are , individually, H or a linear or branched alkyl group with 1 to 10 carbon atoms or an aryl group which is optionally substituted;

R^4 is a n-valent residue of a polyisocyanate of the molecular weight of 150 – 4000 g/mol, particularly of 160 – 1000 g/mol, after removal of n isocyanate groups; and

n = 2, 3, 4, 5 or 6.

Preferably n stands for a value of 2, i.e. the polyoxazolidine **POU** is preferably a bis-oxazolidine.

The substituent R^4 is preferably selected from the group consisting of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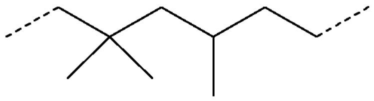
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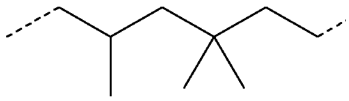

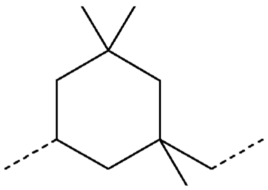
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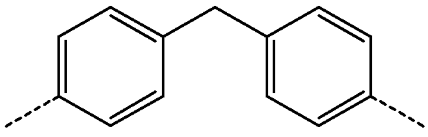
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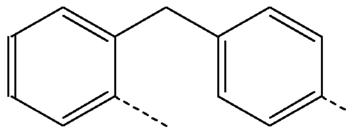

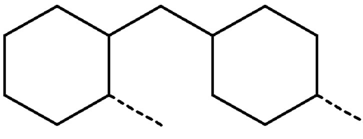
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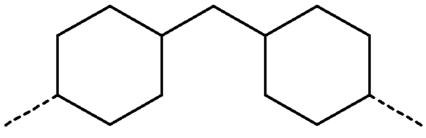
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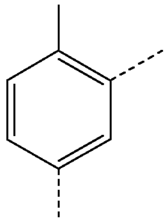
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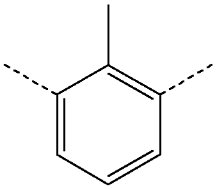
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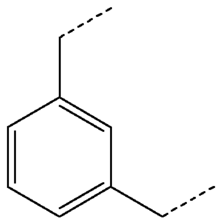
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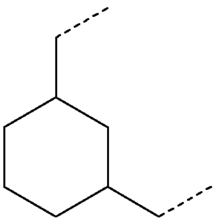
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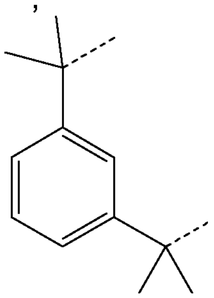
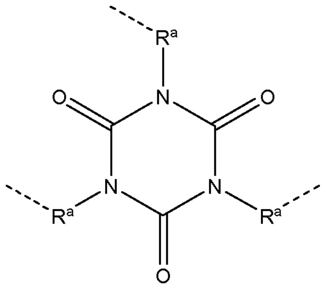
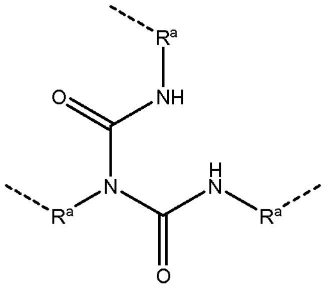
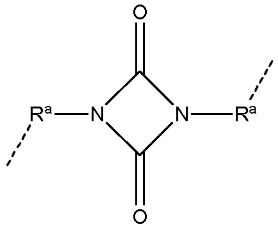


or the isocyanurates or biurets or uretdiones of the corresponding diisocyanates thereof.

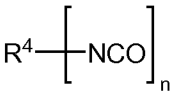
Those substituents R^4 originating from isocyanurates or biurets or uretdiones of the corresponding diisocyanates have particularly one of the following structural formulas:

In these formulas R^a stands for the corresponding diisocyanate after removal of the two NCO groups.

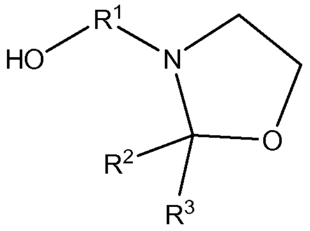
More preferred the substituent R^4 is selected from the group consisting of 1,6-hexamethylene diisocyanate (HDI), 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate or IPDI), 2,4-toluene diisocyanate, 2,6-toluene diisocyanate and the isocyanurates or biurets or uretdiones thereof after removal of n NCO groups.

The polyoxazolidine **POU** having at least two urethane groups is preferably prepared by a reaction of a polyisocyanate, particularly a polyisocyanate of formula (IA), and an oxazolidine having a substituent carrying a hydroxyl group, particularly an oxazolidine of formula (IB), preferably of formula (IB-1).

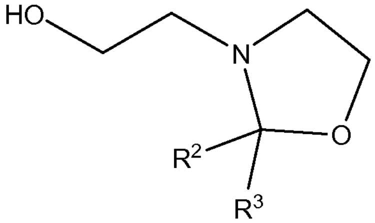


$$R^4\left[-NCO\right]_n$$

(IA)



(IB)



(IB-1)

The oxazolidine having a substituent carrying a hydroxylic group is preferably made from a condensation reaction of an N-hydroalkylethanolamine, particularly of a diethanolamine, and the corresponding ketone R^2COR^3, respectively and preferably the corresponding aldehyde $HCOR^3$.

Suitable polyisocyanates of formula (IA) are particularly 1,6-hexamethylene diisocyanate (HDI), 2-methylpentamethylene 1,5-diisocyanate, 2,2,4- and 2,4,4-trimethyl-1,6-hexamethylene diisocyanate (TMDI), 1,10-decamethylene diisocyanate, 1,12-dodecamethylene diisocyanate, lysine diisocyanate and lysine ester diisocyanate, cyclohexane 1,3- and 1,4-diisocyanate and any desired mixtures of these isomers, 1-methyl-2,4- and -2,6-diisocyanatocyclohexane and any desired mixtures of these isomers (HTDI or H_6TDI), 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (=isophorone diisocyanate or IPDI), perhydro-2,4‘- and -4,4‘-diphenylmethane diisocyanate (HMDI or $H_{12}MDI$), 1,4-diisocyanato-2,2,6-trimethylcyclohexane (TMCDI), 1,3- and 1,4-bis(isocyanatomethyl)cyclohexane, m- and p-xylylene diisocyanate (m- and p-XDI), m- and p-tetramethyl-1,3- and -1,4-xylylene diisocyanate (m- and p-TMXDI), bis(1-isocyanato-1-methylethyl)naphthalene, 2,4- and 2,6-toluene diisocyanate (TDI), 4,4‘-, 2,4'- and 2,2'-diphenylmethane diisocyanate (MDI), 1,3- and 1,4-phenylene diisocyanate, 2,3,5,6-tetramethyl-1,4-diisocyanatobenzene, naphthalene 1,5-diisocyanate (NDI), 3,3'-dimethyl-4,4'-diisocyanatodiphenyl (TODI), dianisidine diisocyanate (DADI), oligomers and polymers of the aforementioned isocyanates, and any desired mixtures of the aforementioned isocyanates. Preference is given to monomeric diisocyanates, especially MDI, TDI, HDI, H_{12}MDI and IPDI.

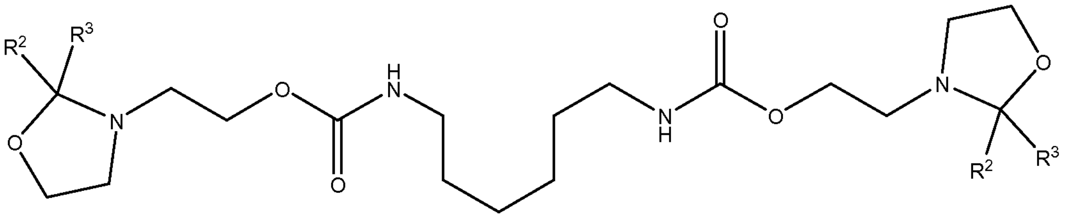
Also suited as polyisocyanate of formula (IA) are the isocyanurates or biurets or uretdiones of the just mentioned polyisocyanates.

Also suited as polyisocyanate of formula (IA) are the isocyanate groups carrying polyurethane prepolymers being a reaction product of aforementioned polyisocyanates with polyols and/or polyamines.

Particularly preferred as polyisocyanate of formula (IA) are selected from the group consisting of 1,6-hexamethylene diisocyanate (HDI), 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate or IPDI), 2,4-toluene diisocyanate, 2,6-toluene diisocyanate.

More preferred polyisocyanates are diisocyanates and most preferred are HDI and TDI.

Most preferred are polyoxazolidines **PUC** which are bis-oxazolidines of formula (IV) or (IV')



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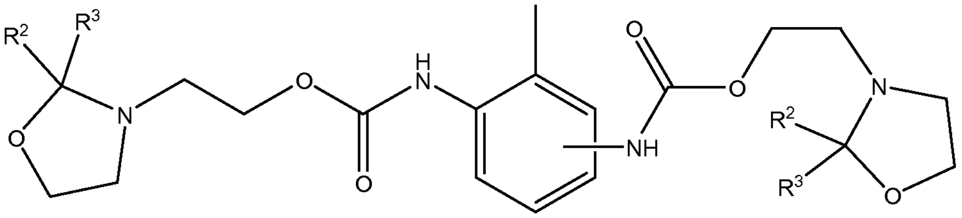


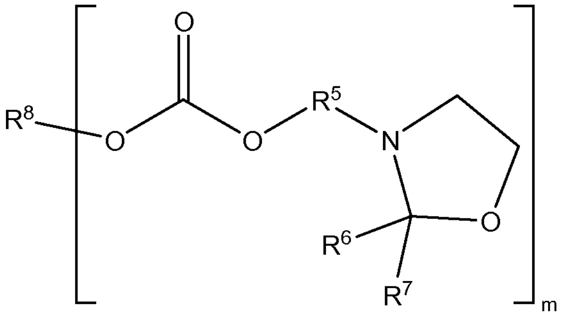
(IV')

R^2 and R^3 being already defined above. R^2 is stands most preferably for H.

The above described polyoxazolidines **POU** having at least two urethane groups are typically liquids at room temperature, which tend to crystallize on storage at low temperature. Typically the crystallization occurs within less than 1 week's time at a temperature of 4°C. Crystallization seeds are known to accelerate this crystallisation process.

The composition comprises at least one polyoxazolidine **POC** having at least one carbonato group.

Preferably the polyoxazolidine **POC** having at least one carbonato group has a structure according to formula (II), particularly to formula (IIa).



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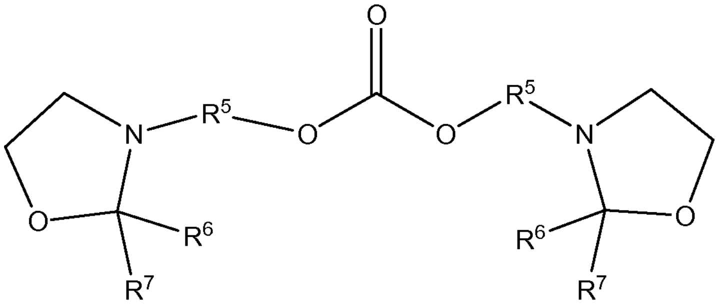


(IIa)

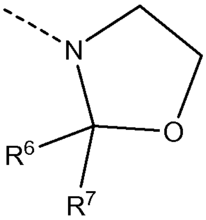
wherein

R^5 is an alkylene group with 2 to 5 carbon atoms, particularly an ethylene group;

R^6 and R^7 are , individually, H or a linear or branched alkyl group with 1 to 6 carbon atoms or an aryl group which is optionally substituted;

m = 1, 2, 3, 4, 5 or 6;

R^8 is a m-valent residue of the molecular weight of 15 – 1000 g/mol, particularly carrying a substituent of the formula (III)

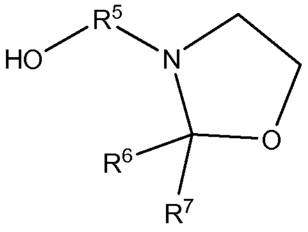


(III).

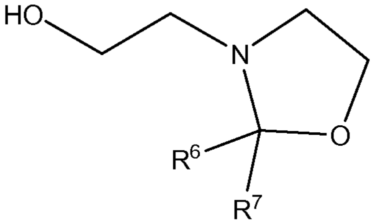
Preferably n stands for a value of 2, i.e. the polyoxazolidine **POC** is preferably a bis-oxazolidine.

The polyoxazolidine **POC** is preferably prepared by a reaction of an organic carbonate, eventually a polyol, particularly a polyol of formula (II A), an oxazolidine having a substituent carrying a hydroxyl group, particularly an oxazolidine of formula (II B), preferably of formula (II B-1).

$$R^8\left[-OH\right]_m \qquad \text{(II A)}$$



(II B)



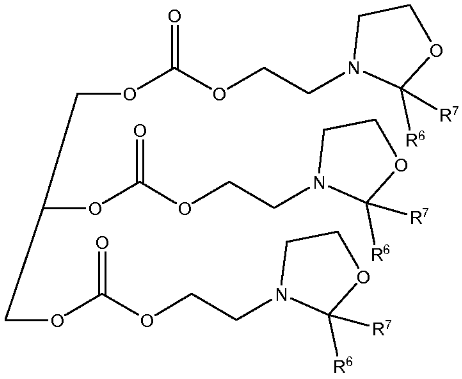
(II B-1)

The details of this reaction and the products thereof formed are described in EP 0 499 188 A1, the entire disclosure of which is hereby incorporated by reference.

Particularly suitable as polyols of formula (IA) are the polyols of the group consisting of 1,2-ethanediol, diethylene glycol, 1,2-propanediol, dipropylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, octanediol, nonanediol, decanediol, neopentyl glycol, pentaerythritol (= 2,2-bis-(hydroxymethyl)-1,3-propanediol), dipentaerythritol (= 3-(3-hydroxy-2,2-bishydroxymethylpropoxy)-2,2-bishydroxymethylpropan-1-ol), glycerol (= 1,2,3-propanetriol), trimethylolpropane (= 2-ethyl-2-(hydroxymethyl)-1,3-propanediol), trimethylolethane (= 2-(hydroxymethyl)-2-methyl-1,3-propanediol), di(trimethylolpropane) (= 3-(2,2-bis(hydroxymethyl)butoxy)-2-ethyl-2-hydroxymethylpropan-1-ol), di(trimethylolethane) (= 3-(3-hydroxy-2-hydroxymethyl-2-methylpropoxy)-2-hydroxymethyl-2-methylpropan-1-ol), diglycerol (= bis(2,3-dihydroxypropyl) ether; cyclohexane-1,2-diyldimethanol, cyclohexane-1,3-diyldimethanol, cyclohexane-1,4-diyldimethanol, 1,2-cyclohexanediol, 1,3-cyclohexanediol, 1,4-cyclohexanediol, 1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane-2,4,6-trione, 2,2',2''-nitrilotriethanol; (poly)ethylene glycols, (poly)propylene glycols and (poly)butylene glycol (= poly(oxy-1,4-butanediyl)-α-hydro-ω-hydroxyl).

The oxazolidine having a substituent carrying a hydroxyl group is preferably made from a condensation reaction of an N-hydroxyalkyl-ethanolamine, particularly of a diethanolamine, and the corresponding ketone R^6COR^7 respectively and preferably the corresponding aldehyde $HCOR^7$.

Preferred polyoxazolidines **POC** are those which are selected from the group consisting of



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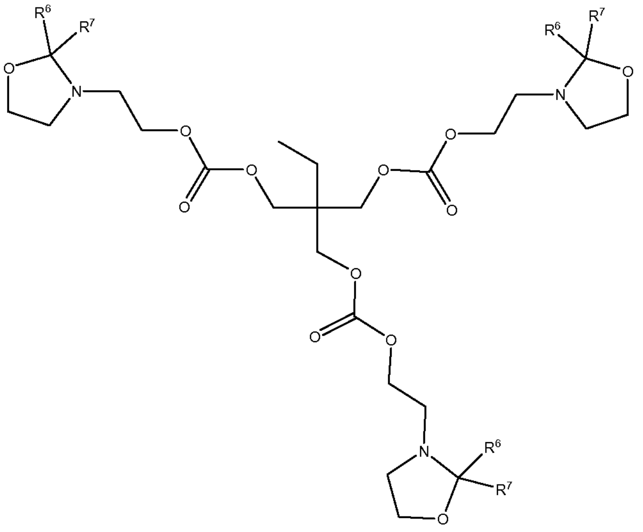

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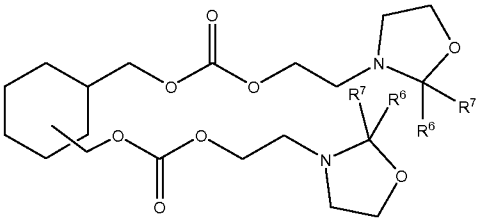

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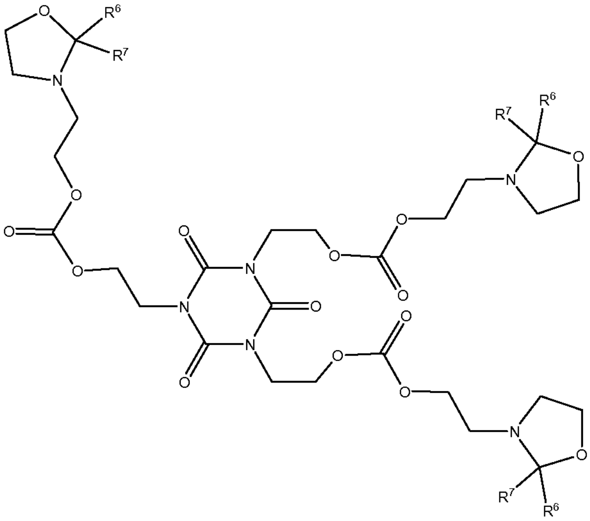

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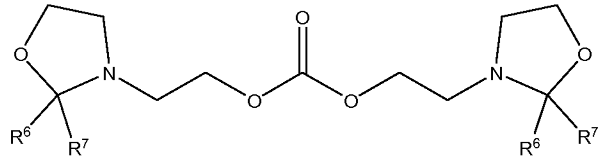


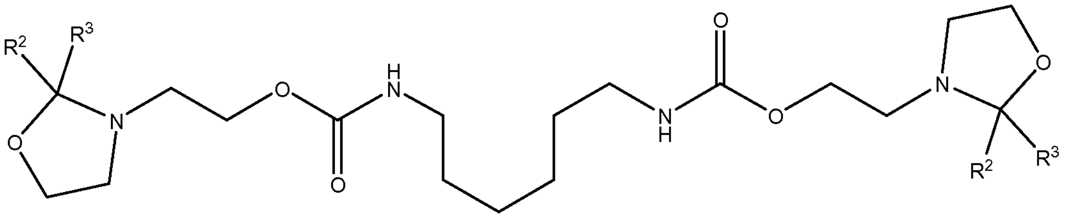
wherein R^6 and R^7 are, individually, H or a linear or branched alkyl group with 1 to 10 carbon atoms or an aryl group which is optionally substituted, preferably a methyl, ethyl or isopropyl group.

The composition of the present invention comprises

a) at least one polyoxazolidine **POU** having at least two urethane groups and

b) at least one polyoxazolidine **POC** having at least one carbonato group.

Preferably the composition comprises or consists of a polyoxazolidine **PUC** which is a bis-oxazolidine of formula (IV) or (IV') and a polyoxazolidine **POC** which is a bis-oxazolidine of formula (V)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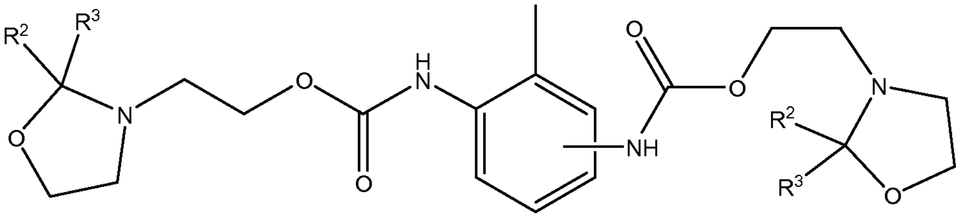
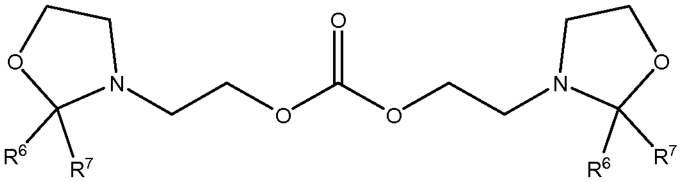
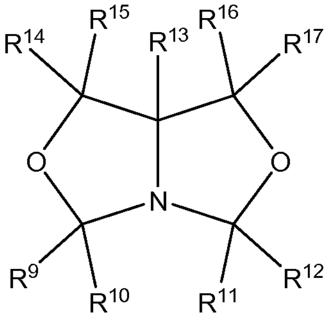

(IV')


(V)

wherein R^2, R^3, R^6 and R^7 are independently from each other H or a linear or branched alkyl group with 1 to 10 carbon atoms, particularly a methyl, ethyl or isopropyl group, preferably an isopropyl group. Preferably R^2 and R^6 are H.

In one embodiment of the invention composition further comprises of at least one bicyclic oxazolidine **BCO.** Preferred bicyclic oxazolidine **BCO** are those having a structure according to formula (VI)


(VI)

wherein R^9, R^{10}, R^{11} and R^{12} are, individually, a linear or branched alkyl group, preferably with 1 to 8 carbon atoms, or a linear or branched hydroxy alkyl group, preferably with 1 to 8 carbon atoms, or an aryl group or a cycloalkyl group, preferably with 6 to 12 carbon atoms;

R^{13} is H or a linear or branched alkyl group, preferably with 1 to 8 carbon atoms, or a linear or branched hydroxy alkyl group, preferably with 1 to 8 carbon atoms;

R^{14}, R^{15}, R^{16} and R^{17} are, individually, H or a linear or branched alkyl group, preferably with 1 to 8 carbon atoms, or a linear or branched hydroxy alkyl group, preferably with 1 to 8 carbon atoms.

Preferably R^9 and R^{11} are H.

The method of preparing such bicyclic oxazolidine **BCO** is known. Particularly described are the details for the method of preparing and details of the products formed in US 5,126,421 and WO 96/08308 A1, the entire disclosure of which is hereby incorporated by reference.

Particularly preferred as bicyclic oxazolidines **BCO** is the compound 1-aza-3,7-dioxo-2,8-diisopropyl-5-ethyl bicyclo[3,3,0]octane, which was comercialised under the tradename ZOLDINE® RD-20 from Angus Chemical Company (Buffalo Grove, USA) and has, therefore, a structure of formula (VI) in which R^9, R^{11}, R^{14}, R^{15}, R^{16} and R^{17} are all H; R^{10} and R^{12} are an isopropyl group and R^{13} is an ethyl group.

Preferably, the amount of all polyoxazolidines **POC** and all of the optionally present bicyclic oxazolidines **BCO** and the sum of all polyoxazolidines **POU** is 80 – 100 % by weight, particularly 90 - 100 % by weight, preferably 95 - 100 % by weight, with regard to the weight of the total composition.

It is preferred that the weight ratio of the sum of all polyoxazolidines **POC** to the sum of all polyoxazolidines **POU** is 5 : 95 – 95 : 5 , particularly 10 : 90 – 45 : 55, preferably 25 : 75 – 35 : 65.

In a first preferred embodiment, the composition is used as a curing agent which is suitable for adding to polyisocyanates or polyurethanes. In this embodiment it is preferred that the composition consists essentially of, preferable consist only of, polyoxazolidine(s) **POC**, polyoxazolidine(s) **POU** and optionally bicyclic oxazolidines(s) **BCO**. Particularly, the composition does not have any solvents, as ingredients. Such curing agent compositions are liquid at room temperature and have in comparison with the polyoxazolidine(s) **POU** a distinctly reduced tendency to crystallise. These compositions have remarkably better storage and transport properties and need less expensive storage equipment or application equipment and are, therefore, very advantageous.

Said compositions are very advantageous over existing polyoxazolidines in that a broad range of non-crystallising curing agents can now be offered, allowing tailoring the curing properties to the customers' needs, particularly by using also commercially known polyoxazolidine(s) **POU** which are prone to crystallization when used as such.

Therefore, in a further aspect of the invention relates to the use of the composition as described before as a non-crystallising curing agent for polyisocyanates.

In a further preferred embodiment, the composition as described before further comprises of a polyisocyanate, particularly a polymer having at least two NCO groups. In other words, this embodiment of the composition corresponds to the composition according to the first embodiment, which has been added to a polyisocyanate or polyurethane composition.

In this embodiment, the amount of all polyoxazolidines **POC** and bicyclic oxazolidines **BCO** and the sum of all polyoxazolidines **POU** is 5 – 20 % by weight, particularly 5 – 15 % by weight, preferably 6 – 10 % by weight, in regard to the weight of the total composition.

As additional polyisocyanates for this embodiment, those polyisocyanates can be used that have been described above for the manufacture of polyoxazolidine **POU** having at least two urethane groups.

Furthermore, polyurethane prepolymers carrying isocyanate groups can be used as additional polyisocyanates. These polyurethane prepolymers are preferably prepared from the above mentioned polyisocyanates and polyols.

Polyols particularly suited for the preparation of polyurethane prepolymers are as follows:

- polyetherpolyols, also known as polyoxyalkylenepolyols or oligoetherols, which are polymerization products of ethylene oxide, 1,2-propylene oxide, 1,2- or 2,3-butylene oxide, oxetane, tetrahydrofuran or mixtures thereof, possibly polymerized with the aid of a initiator molecule with two or more active hydrogen atoms, for example water, ammonia or compounds having a plurality of OH or NH groups, for example 1,2-ethanediol, 1,2- and 1,3-propanediol, neopentyl glycol, diethylene glycol, triethylene glycol, the isomeric dipropylene glycols and tripropylene glycols, the isomeric butanediols, pentanediols, hexanediols, heptanediols, octanediols, nonanediols, decanediols, undecanediols, 1,3- and 1,4-cyclohexanedimethanol, bisphenol A, hydrogenated bisphenol A, 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, glycerol, aniline, and mixtures of the compounds mentioned. It is possible to use either polyoxyalkylenepolyols which have a low degree of unsaturation (measured to ASTM D-2849-69 and reported in milliequivalents of unsaturation per gram of polyol (meq/g)), prepared, for example, with the aid of double metal cyanide complex catalysts (DMC catalysts), or polyoxyalkylenepolyols with a higher degree of unsaturation, prepared, for example, with the aid of anionic catalysts such as NaOH, KOH, CsOH or alkali metal alkoxides.

  Particularly suitable are polyoxyethylenepolyols and polyoxypropylenepolyols, especially polyoxyethylenediols, polyoxypropylenediols, polyoxyethylenetriols and polyoxypropylenetriols.

  Especially suitable are polyoxyalkylenediols or polyoxyalkylenetriols having a degree of unsaturation lower than 0.02 meq/g and having a molecular weight in the range from 1000 to 30 000 g/mol, and also polyoxyethylenediols, polyoxyethylenetriols, polyoxypropylenediols and polyoxypropylenetriols with a molecular weight of 400 to 8000 g/mol. "Molecular weight" or "molar mass" is understood in the present document always to mean the molecular weight average M_n.

Likewise particularly suitable are so-called ethylene oxide-terminated ("EO-endcapped", ethylene oxide-endcapped) polyoxypropylene-polyols. The latter are specific polyoxypropylenepolyoxyethylenepolyols which are obtained, for example, by further alkoxylating pure polyoxypropylenepolyols, especially polyoxypropylenediols and -triols, with ethylene oxide on completion of the polypropoxylation reaction, and have primary hydroxyl groups as a result. Preference is given in this case to polyoxypropylenepolyoxyethylenediols and polyoxypropylenepolyoxyethylenetriols.

- Styrene-acrylonitrile- or acrylonitrile-methyl methacrylate-grafted polyether-polyols.
- PolCterpolyols, also known as oligoesterols, prepared, for example, from di- to trihydric alcohols, for example 1,2-ethanediol, diethylene glycol, 1,2-propanediol, dipropylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, glycerol, 1,1,1-trimethylolpropane or mixtures of the aforementioned alcohols, with organic dicarboxylic acids or the anhydrides or esters thereof, for example succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, dodecanedicarboxylic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid, terephthalic acid and hexahydrophthalic acid, or mixtures of the aforementioned acids, and also polCterpolyols formed from lactones, for example from ε-caprolactone.
- Polycarbonatepolyols, as obtainable by reaction, for example, of the abovementioned alcohols - used to form the polyesterpolyols - with dialkyl carbonates, diaryl carbonates or phosgene.
- Polyacrylate- and polymethacrylatepolyols.
- Poly-hydroxy-functional fats and oils, for example natural fats and oils, especially castor oil; or polyols - known as oleochemical polyols - obtained by chemical modification of natural fats and oils, for example the epoxy polCters or epoxy polyethers obtained by epoxidation of unsaturated oils and subsequent ring opening with carboxylic acids or alcohols, or polyols obtained by hydroformylation and hydrogenation of unsaturated oils; or polyols obtained from natural fats and oils by degradation processes such

as alcoholysis or ozonolysis and subsequent chemical linkage, for example by transesterification or dimerization, of the degradation products or derivatives thereof thus obtained. Suitable degradation products of natural fats and oils are especially fatty acids and fatty alcohols, and also fatty acid esters, especially the methyl esters (FAME), which can be derivatized, for example, by hydroformylation and hydrogenation to hydroxy fatty acid esters.

- Polyhydrocarbonpolyols, also known as oligohydrocarbonols, for example poly-hydroxy-functional ethylene-propylene, ethylene-butylene or ethylene-propylene-diene copolymers, as produced, for example, by Kraton Polymers, or poly-hydroxy-functional copolymers of dienes such as 1,3-butadiene or diene mixtures, and vinyl monomers such as styrene, acrylonitrile or isobutylene, or poly-hydroxy-functional polybutadienepolyols, for example those which are prepared by copolymerization of 1,3-butadiene and allyl alcohol and may also be hydrogenated.
- Poly-hydroxy-functional acrylonitrile/butadiene copolymers, as can be prepared, for example, from epoxides or amino alcohols and carboxyl-terminated acrylonitrile/butadiene copolymers (commercially available under the Hypro® CTBN (formerly Hycar® CTBN) name from Noveon).

These polyols mentioned preferably have a mean molecular weight of 250 – 30 000 g/mol, especially of 1000 - 30 000 g/mol, and preferably have a mean OH functionality in the range from 1.6 to 3.

Particularly suitable polyols are polCterpolyols and polyetherpolyols, especially polyoxyethylenepolyol, polyoxypropylenepolyol and polyoxypropylenepolyoxyethylenepolyol, preferably polyoxyethylenediol, polyoxypropylenediol, polyoxyethylenetriol, polyoxypropylenetriol, polyoxypropylenepolyoxyethylenediol and polyoxypropylenepolyoxyethylenetriol.

In addition to these polyols mentioned, small amounts of low molecular weight di- or polyhydric alcohols, for example 1,2-ethanediol, 1,2- and 1,3-propanediol, neopentyl glycol, diethylene glycol, triethylene glycol, the isomeric dipropylene glycols and tripropylene glycols, the isomeric butanediols, pentanediols, hexanediols, heptanediols, octanediols, nonanediols, decanediols, undecanediols, 1,3- and 1,4-cyclohexanedimethanol, hydrogenated bisphenol A, dimeric fatty alcohols, 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, glycerol, pentaerythritol, sugar alcohols such as xylitol, sorbitol or mannitol, sugars such as sucrose, other higher polyhydric alcohols, low molecular weight alkoxylation products of the aforementioned di- and polyhydric alcohols, and mixtures of the aforementioned alcohols, can be used additionally in the preparation of the polyurethane prepolymer.

These compositions may further comprise other ingredients such as filler, adhesion promoters, stabilizers, thixotropic agents, curing catalysts and other additives which are known to the person skilled in the art of polyurethane compositions.

The filler influences both the rheological properties of the uncured composition, and the mechanical properties and the surface properties of the cured composition. Suitable fillers are inorganic and organic fillers, for example natural, ground or precipitated calcium carbonates which are optionally coated with fatty acids, especially stearates, barium sulfate ($BaSO_4$, also known as barite or heavy spar), calcined kaolins, quartz flour, aluminum oxides, aluminum hydroxides, silicas, especially high-dispersity silicas from pyrolysis processes, carbon blacks, especially industrially produced carbon black, PVC powders or hollow spheres. Preferred fillers are barium sulfate and calcium carbonates, carbon black and flame-retardant fillers such as hydroxides or hydrates, especially hydroxides or hydrates of aluminum, preferably aluminum hydroxide.

These compositions cure very rapidly and have advantages particularly in that the curing behaviour can be easily varied by the choice of the structures of polyoxazolidine(s) **PUC** and polyoxazolidine(s) **POC**.

The compositions can be used in a broad scope of applications, particularly as coatings, adhesives, sealants, as compositions for flooring or for molding.

These compositions are particularly suited to be used in the field of repair, civil engineering and industrial manufacturing of goods, particularly in the manufacturing of vehicles such as cars.

Examples

The following examples serve to illustrate the invention described above.

Synthesis of 2-(2-isopropyloxazolidin-3-yl)ethanol (***i-Pr-OE***)

1495.07 g (14.2 moles) diethanolamine and 400g of light petroleum naphtha solvent were added to a 5 litre reaction flask equipped with a stirrer and reflux condenser. The mixture was heated to 40°C using a heating mantle and 1104.9 g (15.3 moles) of isobutyraldehyde slowly added over a period of 1 hour, whilst maintaining the reaction temperature below 60°C. Once all of the isobutyraldehyde had been added, Dean and Stark apparatus was added to the reaction vessel and the mixture heated to 85°C. The reaction was maintained between 80-85°C until 254.3 g of water had distilled off. The reaction temperature was then raised to 125°C and the solvent and excess isobutyraldehyde distilled off under reduced pressure (approx. 0.8 bar).

The resultant 2-(2-isopropyloxazolidin-3-yl)ethanol (***i-Pr-OE***) was isolated as a yellow oil with a purity of 97.1 % (determined by GC).

Synthesis of polyoxazolindine ***POU-1***

994.6g (6.3 moles) of 2-(2-isopropyloxazolidin-3-yl)ethanol (***i-Pr-OE***) and 0.12g DBTDL catalyst were added to a 1 litre reaction vessel. 335.5g (1.9 moles) of toluene diisocyanate (Desmophen T80) (a 80:20 mixture of 2,4- and 2,6-toluene diisocyanate) was added dropwise over a 2 hour period. The reaction mixture was held at 90-100°C for 1.5 - 2 hours using gentle heating. End of reaction was determined by IR analysis and the disappearance of the NCO peak at 2275cm^{-1}. The final bis-oxazolidine product ***POU-1*** was isolated as a viscous pale yellow liquid with a viscosity of 21.4 Pa•s (214 P) determined by Brookfield at 20ºC.

Synthesis of polyoxazolindine ***POC-1***

1081.98g (6.8 moles) of 2-(2-isopropyloxazolidin-3-yl)ethanol (***i-Pr-OE***), 912.9g (10.1 moles) dimethyl carbonate and 5.12g of potassium tert-butoxide were added to a 2 litre reaction flask equipped with a reflux condenser and heated to 80°C. The transesterification was carried out for 6 hours at 80-100°C under nitrogen after which the batch was set-up for reflux and the methanol removed between 80-130°C. 112.3g methanol was collected. Excess mass collected was attributed to excess dimethyl carbonate. The final bis-oxazolidine ***POC-1*** was isolated as a free flowing yellow liquid with a viscosity of 48.2 mPa•s (48.2 cP) (method used see above: synthesis of ***POU-1***) with a purity of 77% (determined by GC).

Synthesis of polyoxazolidine ***POU-2***

668.8g (4.2 moles) of 2-(2-isopropyloxazolidin-3-yl)ethanol (***i-Pr-OE***) and 0.08g DBTDL catalyst were added to a 1 litre reaction vessel. 331.1 g (2.0 moles) of hexamethylene 1,6-diisocyanate (HDI) was added dropwise over a 1.5 hour period whilst maintaining the reaction temperature below 100°C. The reaction mixture was then held at 90-1 OO°C for 2 hours using gentle heating. End of reaction was determined by IR analysis and the disappearance of the NCO peak at 2275cm^{-1}. The final bis-oxazolidine product ***POU-2*** was isolated as a viscous yellow liquid with a viscosity of 15.4 Pa•s (154 P) (method used see above: synthesis of ***POU-1***).

Storage stability tests

The polyoxazolidines respectively the mixtures (being prepared by mixing the two polyoxazolidines in the mixing ratio indicated in table 1 in a mixing vessel under nitrogen during 30 minutes at 60°C) were tested in view of their storage stability, respectively on their tendency to crystallize.

For this the examples of comparison (***Ref.1***, ***Ref.2*** and ***Ref.3***) as well as the examples (***1***, ***2***, ***3*** and ***4***) are individually stored in sealed containers at 4°C and at -12.5°C. The samples were checked regularly to determine whether or not they have crystallized. In table 1 it was indicated if the sample has been crystallized (“C”) or not crystallized (“NC”) or partly crystallized (“PC”)

In a further series of experiment a few crystals of ***POU-2*** were added initially as crystallization seeds to each of the different samples and the crystallization behaviour was checked analogously.

	Ref.1	***Ref.2***	***1***	***2***	***3***	***4***	***5***
POU-1 [% by weight]	100		90	80	75	65	
POU-2 [% by weight]		100					80
POC-1 [% by weight]			10	20	25	35	20
Storage Stability							
non-seeded							
1 day at 4°C	C	C	NC	NC	NC	NC	NC
1 week at 4°C	C	C	NC	NC	NC	NC	NC
2 weeks at 4°C	C	C	NC	NC	NC	NC	NC
1 month at 4°C	C	C	NC	NC	NC	NC	PC
6 months at 4°C	C	C	NC	NC	NC	NC	C
12 months at 4°C	C	C	NC	NC	NC	NC	C
1 day at -12.5°C	C	C	NC	NC	NC	NC	NC
1 week at -12.5°C	C	C	NC	NC	NC	NC	PC
2 weeks -12.5°C	C	C	NC	NC	NC	NC	C
1 month -12.5°C	C	C	NC	NC	NC	NC	C
6 months -12.5°C	C	C	NC	NC	NC	NC	C
12 months -12.5°C	C	C	NC	NC	NC	NC	C
seeded							
1 day at 4°C, seeded	C	C	NC	NC	NC	NC	NC
1 week at 4°C, seeded	C	C	NC	NC	NC	NC	PC
2 weeks at 4°C, seeded	C	C	NC	NC	NC	NC	C
1 month at 4°C, seeded	C	C	NC	NC	NC	NC	C
6 months at 4°C, seeded	C	C	NC	NC	NC	NC	C
12 months at 4°C, seeded	C	C	NC	NC	NC	NC	C
1 day at -12.5°C, seeded	C	C	NC	NC	NC	NC	NC
1 week at -12.5°C, seeded	C	C	NC	NC	NC	NC	C
2 weeks -12.5°C, seeded	C	C	NC	NC	NC	NC	C
1 month -12.5°C, seeded	C	C	NC	NC	NC	NC	C
6 months -12.5°C, seeded	C	C	NC	NC	NC	NC	C
12 months -12.5°C, seeded	C	C	NC	NC	NC	NC	C

Table 1. compositions and storage stability.

The results of table 1 show that the examples ***1, 2*** and ***3*** have a much better storage stability as compared to the polyoxazolidines having at least two urethane groups alone (***Ref.1*** and ***Ref.2***).

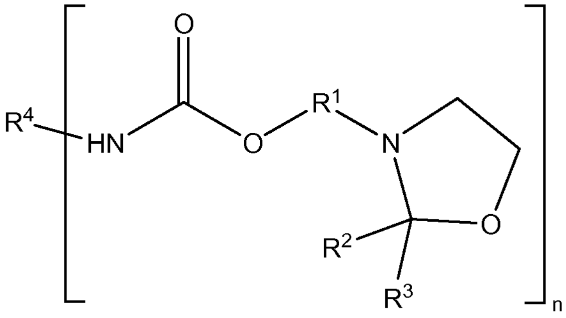
Patent Claims

1. Composition comprising

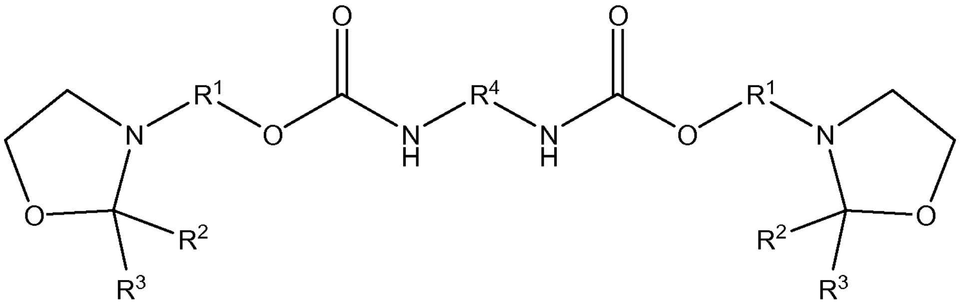
   a) at least one polyoxazolidine **POU** having at least two urethane groups and

   b) at least one polyoxazolidine **POC** having at least one carbonato group.

2. Composition according to claim 1, characterized in that the polyoxazolidine **POU** has a structure according to formula (I), particularly to formula (Ia),



(I)



(Ia)

wherein

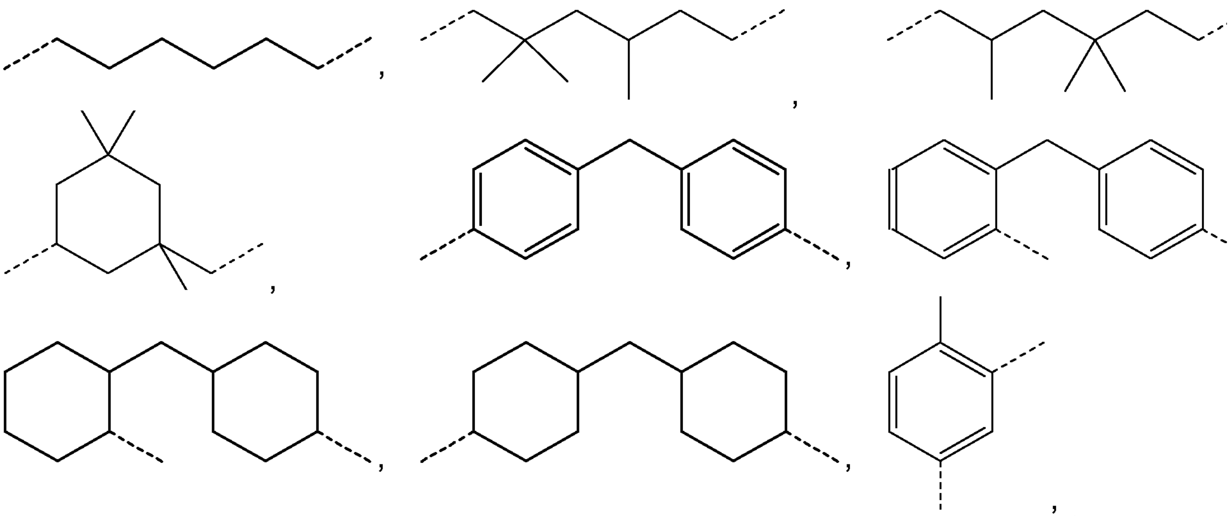
R^1 is an alkylene group with 2 to 5 carbon atoms, particularly an ethylene group;

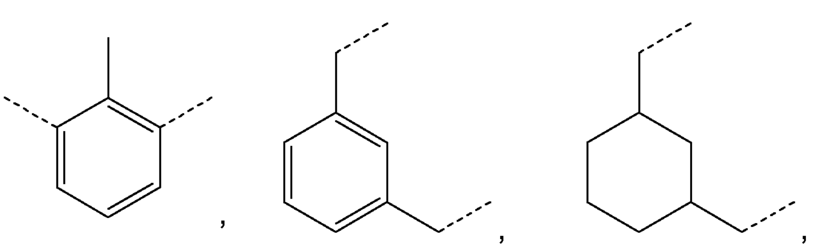
R^2 and R^3 are , individually, H or a linear or branched alkyl group with 1 to 10 carbon atoms or an aryl group which is optionally substituted;

R^4 is a n-valent residue of a polyisocyanate of the molecular weight of 150 – 4000 g/mol, particularly of 160 – 1000 g/mol, after removal of n isocyanate groups; and

n = 2, 3, 4, 5 or 6.

3. Composition according to claim 2, characterized in that R^4 is selected from the group consisting of





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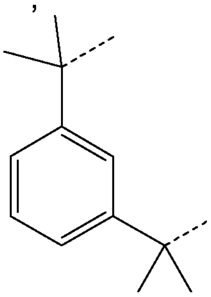
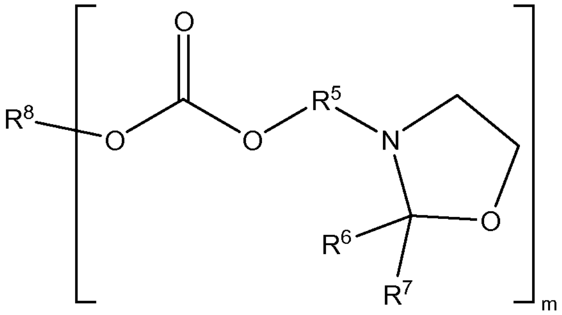


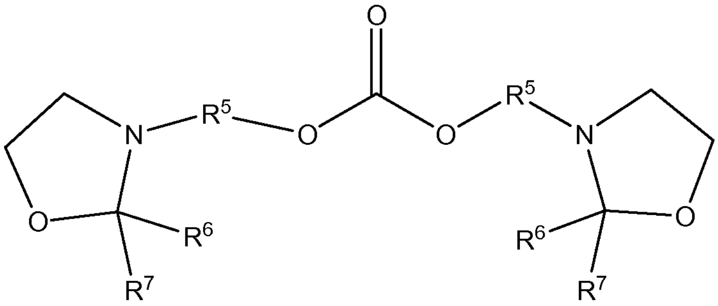
or the isocyanurates or biurets or uretdiones of the corresponding diisocyanates thereof.

4. Composition according to claim 2 or 3, characterized in that R^4 is selected from the group consisting of 1,6-hexamethylene diisocyanate (HDI), 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate or IPDI), 2,4-toluene diisocyanate, 2,6-toluene diisocyanate and the isocyanurates or biurets or uretdiones thereof after removal of n NCO groups.

5. Composition according to any one of the preceding claims, characterized in that the polyoxazolidine **POC** has a structure according to formula (II), particularly to formula (IIa)



(II)



(IIa)

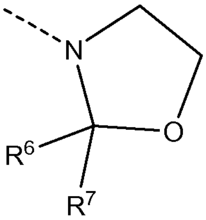
wherein

R^5 is an alkylene group with 2 to 5 carbon atoms, particularly an ethylene group;

R^6 and R^7 are , individually, H or a linear or branched alkyl group with 1 to 6 carbon atoms or an aryl group which is optionally substituted;

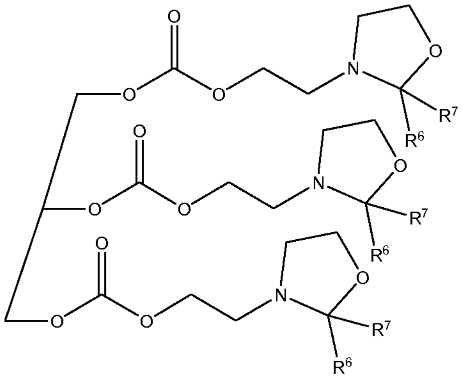
m = 1, 2, 3, 4, 5 or 6; particularly 2;

R^8 is a m-valent residue of the molecular weight of 15 – 1000 g/mol, particularly carrying a substituent of the formula (III)



(III).

6. Composition according to any one of the preceding claims, characterized in that the polyoxazolidine **POC** is selected from the group consisting of



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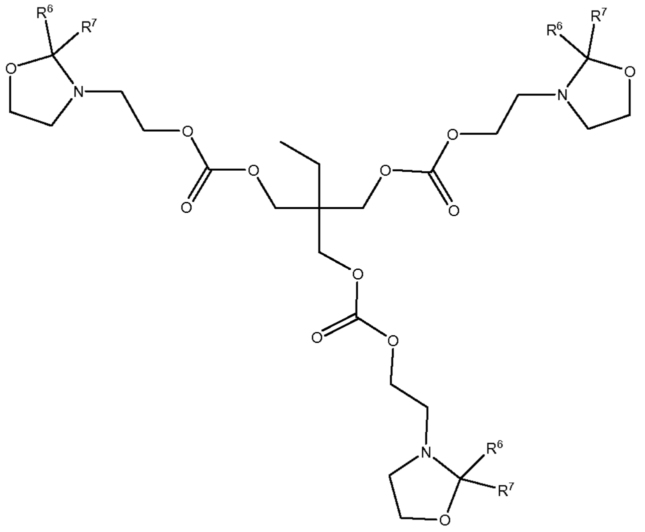

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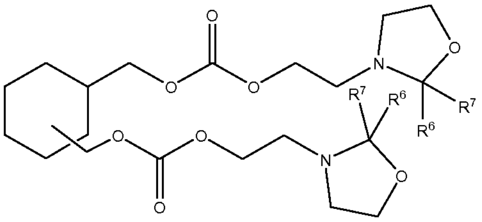

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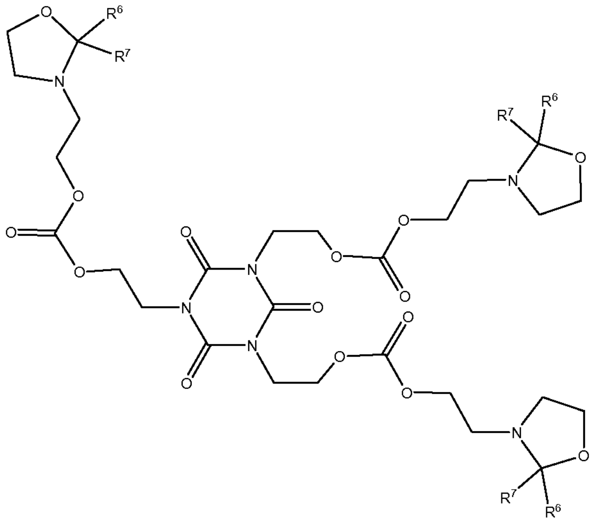

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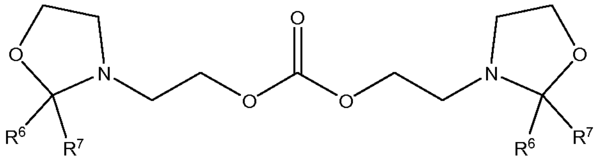
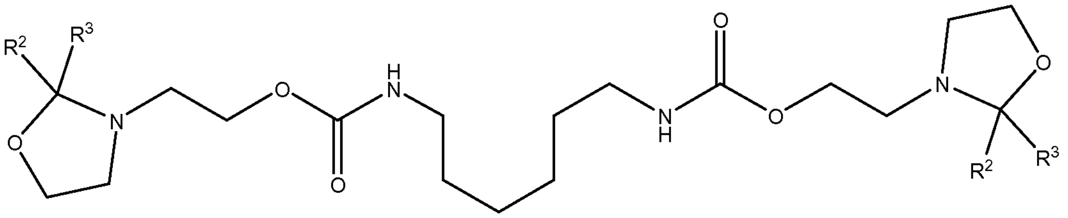
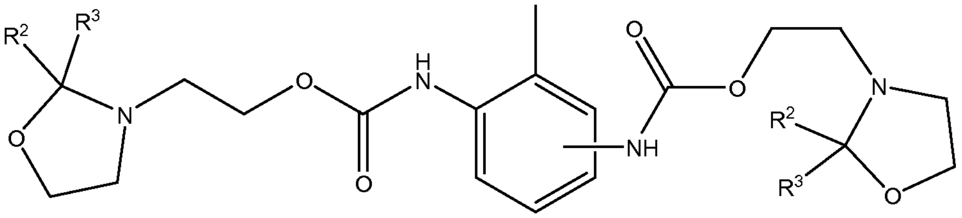


wherein R^6 and R^7 are, individually, H or a linear or branched alkyl group with 1 to 10 carbon atoms or an aryl group which is optionally substituted, preferably a methyl, ethyl or isopropyl group.

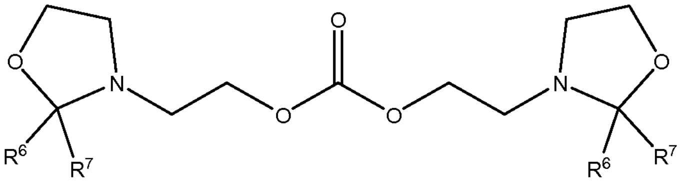
7. Composition according to any one of the preceding claims, characterized in that the polyoxazolidines **PUC** is a bis-oxazolidines of formula (IV) or (IV') and the polyoxazolidines **POC** is a bis-oxazolidines of formula (V)



(IV)



(IV')



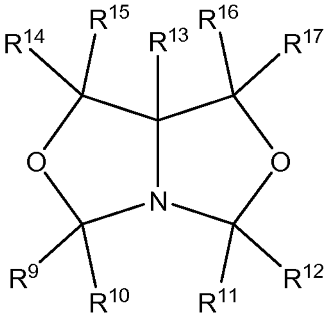
(V)

wherein R^2, R^3, R^6 and R^7 are independently from each other H or a linear or branched alkyl group with 1 to 10 carbon atoms, particularly a methyl, ethyl or isopropyl group, preferably a isopropyl group.

8. Composition according to any one of the claims 2 to 7, characterized in that R^2 and R^6 are H.

9. Composition according to any one of the preceding claims, characterized in that the composition further comprises at least one bicyclic oxazolidine **BCO.**

10. Composition according to claim 9, characterized in that the bicyclic oxazolidine **BCO** has a structure according to formula (VI)



(VI)

wherein R^9, R^{10}, R^{11} and R^{12} are, individually, a linear or branched alkyl group, preferably with 1 to 8 carbon atoms, or a linear or branched hydroxy alkyl group, preferably with 1 to 8 carbon atoms, or an aryl group or a cycloalkyl group, preferably with 6 to 12 carbon atoms;

R^{13} is H or a linear or branched alkyl group, preferably with 1 to 8 carbon atoms, or a linear or branched hydroxy alkyl group, preferably with 1 to 8 carbon atoms;

R^{14}, R^{15}, R^{16} and R^{17} are, individually, H or a linear or branched alkyl group, preferably with 1 to 8 carbon atoms, or a linear or branched hydroxy alkyl group, preferably with 1 to 8 carbon atoms.

11. Composition according to any one of the preceding claims, characterized in that the amount of all polyoxazolidines **POC** and all of the optionally present bicyclic oxazolidines **BCO** and the sum of all polyoxazolidines **POU** is 80 – 100 % by weight, particularly 90 - 100 % by weight, preferably 95 - 100 % by weight, in regard to the weight of the total composition.

12. Composition according to any one of the preceding claims, characterized in that the weight ratio of the sum of all polyoxazolidines **POC** to the sum of all polyoxazolidines **POU** is 5 : 95 – 95 : 5 , particularly 10 : 90 – 45 : 55, preferably 25 : 75 – 35 : 65.

13. Composition according to any one the claims 1 - 12, characterized in that the composition comprises further a polyisocyanate, particularly a polymer having at least two NCO groups.

14. Composition according to claim 13, characterized in that the amount of all polyoxazolidines **POC** and bicyclic oxazolidines **BCO** and the sum of all polyoxazolidines **POU** is 5 – 20 % by weight, particularly 5 - 15 % by weight, preferably 6 – 10 % by weight, in regard to the weight of the total composition.

15. Use of the composition according to any one of the claims 1 to 12 as a non-crystallising curing agent for polyisocyanates.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/065998

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/28 C08G64/02 C07D413/12 C07D263/04
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 C07D

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 practical, search terms used)

EPO-Internal, WPI Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 977 285 A (ERNST MOOS JAN WILHELM [US] ET AL) 2 November 1999 (1999-11-02) cited in the application column 3, line 26 - column 5, line 56 -----	1-15
A	GB 1 463 944 A (BAYER AG) 9 February 1977 (1977-02-09) cited in the application claim 1 -----	1-15
A	EP 0 499 188 A1 (ENICHEM SINTESI [IT] ENICHEM SPA [IT]) 19 August 1992 (1992-08-19) cited in the application claims 1, 10 -----	1-15

☐ 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

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"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 3 December 2010	Date of mailing of the international search report 09/12/2010
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 Lewis, Sara

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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