(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
28 May 2009 (28.05.2009)

PCT

(10) **International Publication Number**
WO 2009/065873 A2

(51) **International Patent Classification:**
C09D 175/08 (2006.01) ***C08G 18/79*** (2006.01)
C08G 18/24 (2006.01) ***B01J 23/14*** (2006.01)
C08G 18/48 (2006.01)

(21) **International Application Number:**
PCT/EP2008/065869

(22) **International Filing Date:**
19 November 2008 (19.11.2008)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
07121179.1 21 November 2007 (21.11.2007) EP

(71) **Applicant** *(for all designated States except US)*: **BASF SE** [DE/DE]; 67056 Ludwigshafen (DE).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: **MEHTA, Bir Darbar** [IN/SG]; 57C Hong Leong Garden Condominium, Block 6, West Coast Drive, 127983, Singapore (SG). **JAFFAR ALI, Malik Jamal** [IN/SG]; Block 668, #13-24, Chander Road, Singapore 210668 (SG). **FECHTENKÖTTER, Andreas** [DE/SG]; #04-35 Caribbean, 24 Keppel Bay Drive, Singapore 098647 (SG). **PENG, Chih-Cheng** [—/SG]; #03-04, 42 South Buona Vista Road, Singapore 118166 (SG).

(74) **Common Representative: BASF SE**; 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, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

(54) **Title:** POLYHEDRAL OLIGOMERIC STANNASILSESQUIOXANES AS CATALYST FOR POLYURETHANE CURING

(57) **Abstract:** The invention relates to a curable composition comprising the following components: (A) at least one isocyanate, (B) at least one binder, and (C) at least one polyhedral oligomeric silsesquioxane, with the number of cages z per molecule being 2 or 3 and the number of tin atoms per molecule being at least one. Furthermore, the invention refers to a kit of parts comprising as components A), B), and C); to the use of the polyhedral oligomeric silsesquioxanes in coatings, lacquers, paintings, films and polymer compositions; to coatings obtainable by curing of these compositions; and to the use of polyhedral oligomeric silsesquioxanes containing at least one metal atom, in particular polyhedral oligomeric stannasilsesquioxane to increase the scratch resistance of coatings.

WO 2009/065873 A2

Polyhedral oligomeric stannasilsesquioxanes as catalyst for polyurethane curing

Description

The invention relates to a curable composition comprising the following components:

(A) at least one isocyanate,
(B) at least one binder, and
(C) at least one polyhedral oligomeric silsesquioxane, with the number of cages z per molecule being 2 or 3 and the number of tin atoms per molecule being at least one.

Furthermore, the invention refers to a kit of parts comprising as components A), B), and C); to the use of the polyhedral oligomeric silsesquioxanes in coatings, lacquers, paintings, films and polymer compositions; to coatings obtainable by curing of these compositions; and to the use of polyhedral oligomeric silsesquioxanes containing at least one metal atom, in particular polyhedral oligomeric stannasilsesquioxane to increase the scratch resistance of coatings.

Coating applications are becoming increasingly more demanding in terms of performance, safety and environmental compliance. Coatings based on isocyanates and binders, i.e., components containing hydrogen atoms reactive to isocyanates, in the following referred to as polyurethane coatings, are known to provide high chemical resistance, flexibility, abrasion resistance, weathering and impact resistance. The protection afforded by such coatings is of particular significance in the automotive, construction, marine and chemical sectors.

Polyurethane coatings or films can for instance be made by reacting multifunctional hydroxyl or amino group containing compounds (polyols or polyamines) and multifunctional isocyanates (polyisocyanates) by means of an isocyanate addition polymerization process. The reaction between the isocyanate groups (NCO) and the active hydrogen atoms of the binder is usually accelerated by the means of catalysts.

Generally a distinction can be made between one-component (1K) and two-component (2K) coating materials. Two-component coating materials are not mixed until shortly before application and thus have only a limited processability time. Systems of this kind are distinguished by rapid curing after the components have been mixed. One-component systems, in contrast, have a long pot life (i.e., the length of time that a catalyzed resin system retains a viscosity low enough to be used in processing). This has been achieved to date, for example, by blocking the NCO groups. But when such coatings are cured, the blocking agents escape.

Two-component curable mixtures comprising polyisocyanates and binders, in particular binders based on polyols or polyamines, are well-known in the art to provide excellent performance and cure at low temperatures. However, due to the reactivity of the isocyanates and the binder, it is often difficult to obtain long pot lives of the mixture of the polyisocyanate and the binder and yet still enjoy the benefits of rapid cure. This is especially true for low VOC materials, which will incorporate relatively low levels of solvent.

The catalysis of isocyanate addition reactions plays an important part in technical polyurethane chemistry such as the production of polyurethane foams, elastomers, lacquers, coatings and adhesives.

Tertiary amines and metal compounds have been used as catalysts, examples being triethylene diamine, tin(II)-octoate and di-n-butyl tin dilaurate. These compounds catalyze urethane formation (reaction of isocyanate groups with alcoholic hydroxyl groups) and urea formation (reaction of isocyanate groups with water) as well as the trimerization of isocyanate groups, addition of isocyanate groups to urethane groups (allophanate formation) and addition of isocyanate groups to urea groups (biuret formation).

Organic tin compounds are frequently used as catalysts in both, one component and two component polyurethane systems. A survey of the catalysts commonly used and the mechanism of their action may be found in A. Farkas and G. A. Mills, Advan. Catalysis, 13, 393 (1962), J. H. Saunders and K. C. Frisch, Polyurethanes, Part I, Wiley Interscience, New York, 1962, Chapter VI, and K. C. Frisch and L. P. Rumao, J. Macromol, Sci. Revs. Macromol Chem., C5(1), 103-150 (1970).

Amines often exhibit insufficient catalytic activity, odor, and toxicity. Catalytically active tin compounds known from the prior art, in particular tin carboxylates and tin alkoxides also have several disadvantages.

First, these active tin compounds are sensitive to hydrolysis. Therefore, they cannot readily be incorporated in the usual polyol formulations, which generally contain traces of moisture because they would gradually lose at least some of their catalytic activity when stored in the polyol formulations.

A second disadvantage of these active tin compounds is that when they are used in combination with (poly)isocyanates, they should be incorporated only shortly before the systems are applied because their presence would seriously impair the storage stability of the polyisocyanates due to the above-mentioned side reactions which are catalyzed by tin compounds.

In addition, organo-tin catalysts have recently come under increasing pressure from users on account of toxicological concerns. Accordingly there is an increasing demand for more toxicologically favorable alternatives to the organo-tin catalysts.

It is known that particulate material (e.g. calcium carbonate, silica, carbon black, etc.) can be incorporated into a polymer to control both polymer morphology and the resulting physical properties. Further it is known that the catalysts used to promote the curing reaction influence the resulting physical properties of the resulting polymers.

It has been suggested recently to use polyhedral oligomeric metallo silsesquioxanes (POMS) as both, cure promoter and nanosized filler in cured polymer compositions. Like the all silicon containing polyhedral oligomeric silsesquioxane (POSS) cages, POMS contain internal frameworks that are primarily comprised of inorganic silicon-oxygen bonds but which also contain one or more metal atoms bound to or inside of the cage.

Metal-containing silasesquioxanes have recently been discussed in view of their possible use as catalysts (Abbenhuis, Chem. Eur. J. 2000, 6, 25-32). Metal silasesquioxanes have been used, for example, as homogeneous catalysts for olefin metathesis (Feher et al., J. Am. Chem. Soc. 1994, 116, 2145-2146) and olefin polymerization (Feher et al., J. Chem. Soc., Chem. Commun. 1990, 1614-1616).

WO-2007/041344 describes metallized polyhedral oligomeric silsesquioxanes and metallized polyhedral oligomeric silicates as cure promoters, catalysts and alloying agents for the reinforcement of polymers. As polymers, a plurality of crosslinkable polymer systems are mentioned. The nanostructured chemicals can be incorporated into the polymer via blending or mixing with the polymer or its precursors.

In particular, WO-2007/041344 discloses in Figure 5 several preferred POSS structures containing Ti, Zn or Al as cure promoters and catalysts for polyurethanes. As an example, the cure of a two-component polyurethane is disclosed with a $[(RSiO_{1.5})_7(MeSiO)(i\text{-}propylO)_2TiO_{0.5}]$ system leading to a smooth surface coating with optical transparency and minimal color. It is mentioned that the before-mentioned Ti-containing POSS structures exhibit excellent hydrophilic stability. It is also mentioned that POMS derivatives containing Sn are also highly active toward polyurethane cure.

However, WO-2007/041344 does not disclose any specific tin-containing POSS structures, nor does it disclose any information on the impact of tin-containing POSS on the properties of the resulting coatings.

It was an object of the present invention to provide curable compositions comprising isocyanates which have an extended pot life and high storing stability. Furthermore, the curing time of the curable compositions ought to be short. The efficiency of the catalyst used ought to be high. The formulation ought to be homogeneous and easy to disperse. The drying process ought to proceed without problems leading to coatings and/or films with high optical quality.

It was yet another object of the present invention to provide curable compositions based on isocyanates leading to coatings with high scratch resistance. The coatings furthermore ought to be resistant to chemicals and weathering. The corresponding surface ought to be of high optical quality. The coatings ought to exhibit sufficient flame retardancy and excellent mechanical performance characteristics.

It was yet another object of the present invention to provide coatings exhibiting low VOC (volatile organic component). In particular, the VOC due to any catalyst ought to be zero. The composition ought to contain no volatile heavy metal compounds, in particular no volatile organometallic compound. The catalyst used to promote the curing reaction ought to exhibit low toxicity and ought to be less sensitive to hydrolysis.

It was yet another objective to provide catalysts for isocyanate curing with lower toxicity and to provide an environmentally friendly urethane reaction catalyst having effectiveness as a reaction catalyst without using a toxic compound and to provide a two-part type urethane coating composition using the catalyst.

In addition, for coating compositions, especially clearcoat or topcoat compositions, it is desired that the coating have a high degree of scratch resistance to protect the appearance of the coating system as a whole.

The present invention provides a two-component curable mixture which, in some applications as a coating composition, has improved scratch resistance over other two-component curable mixtures comprising polyisocyanates and active hydrogen containing resins. The curable composition as provided herein also provides excellent performance characteristics at low temperatures and has an extended pot life.

The curable compositions according to this invention comprise a component (A) containing at least one isocyanate (subsequently referred to as isocyanate component (A)), a component (B) containing at least one binder (subsequently referred to as binder component (B)), and at least one polyhedral oligomeric silsesquioxane with the number of cages z per molecule being 2 or 3 and the number of tin atoms per molecule being at least one as component (C).

Isocyanate component (A)

Isocyanates suitable for the present invention are known to the person skilled in the art or can be synthesized according to methods known to the person skilled in the art.

An isocyanate for the purpose of the present invention is an organic molecule containing at least one –NCO group per molecule. If the isocyanate molecule contains two – NCO groups, it is a diisocyanate. An isocyanate containing two or more isocyanate groups or an isocyanate representing a mixture of different isocyanates, where the number average of isocyanate groups per molecule is at least 2, is referred to as polyisocyanate throughout this invention.

It is preferred if isocyanate component (A) is a polyisocyanate. Preferably isocyanate component (A) has an average number of at least 2 NCO groups per molecule (number-weighted average).

Preferably, component (A) contains at least one oligomer of at least one diisocyanate. As parent diisocyanates preferably diisocyanates having from 4 to 20 carbon atoms are used. In principle, the parent diisocyanates can be used as such or as mixture with oligomers. Preferably, however, diisocyanates are used in oligomeric form.

Examples of conventional diisocyanates are aliphatic diisocyanates, such as tetramethylene diisocyanate, 1,5-pentamethylene diisocyanate, hexamethylene diisocyanate (1,6-diisocyanatohexane), octamethylene diisocyanate, decamethylene diisocyanate, dodecamethylene diisocyanate, tetradecamethylene diisocyanate, derivatives of lysine diisocyanate, trimethylhexane diisocyanate or tetramethylhexane diisocyanate, cycloaliphatic diisocyanates, such as 1,4-, 1,3- or 1,2-diisocyanatocyclohexane, 4,4'- or 2,4'-di(isocyanatocyclohexyl)methane, 1-isocyanato-3,3,5-trimethyl-5-(isocyanatomethyl)cyclohexane (isophoronediisocyanate), 1,3- or 1,4-bis(isocyanatomethyl)cyclohexane or 2,4- or 2,6-diisocyanato-1-methylcyclohexane, and 3(or 4),8(or 9)-bis(isocyanatomethyl)tricyclo[5.2.1.02,6]decane isomer mixtures, and aromatic diisocyanates, such as toluene 2,4- or 2,6-diisocyanate and the isomer mixtures thereof, m- or p-xylylene diisocyanate, 2,4'- or 4,4'-diisocyanatodiphenylmethane and the isomer mixtures thereof, phenylene 1,3- or 1,4-diisocyanate, 1-chlorophenylene 2,4-diisocyanate, naphthylene 1,5-diisocyanate, biphenylene 4,4'-diisocyanate, 4,4' diisocyanato-3,3'-dimethylbiphenyl, 3-methyldiphenylmethane 4,4'-diisocyanate, tetramethylxylylene diisocyanate, 1,4-diisocyanatobenzene or 4,4'-diisocyanatodiphenyl ether.

Also suitable in principle are higher isocyanates, having on average more than 2 isocyanate groups. Examples that are suitable include triisocyanates such as triisocyanatononane, 2,4,6-triisocyanatotoluene, triphenylmethane triisocyanate or 2,4,4’-

triisocyanato-diphenyl ether, or the mixtures of diisocyanates, triisocyanates and higher polyisocyanates that are obtained by phosgenating corresponding aniline/formaldehyde condensates and represent polyphenyl polyisocyanates containing methylene bridges.

Cycloaliphatic and aliphatic diisocyanates are preferred. Particularly preferred are 1-isocyanato-3,3,5-trimethyl-5-(isocyanatomethyl)-cyclohexane (isophorone diisocyanate), 1,6 diisocyanatohexane, 4,4'-di(isocyanatocyclohexyl)methane, and 3(or 4),8(or 9)-bis(isocyanatomethyl)tricyclo[5.2.1.02,6]decane isomer mixtures.

Component (A) may comprise polyisocyanates and polyisocyanate-containing mixtures which contain biuret, urethane, allophanate and/or isocyanurate groups, preferably polyisocyanates containing isocyanurate groups and/or polyisocyanates containing allophanate groups. Particular preference is given to polyisocyanates comprising predominantly isocyanurate groups. With very particular preference the fraction of the isocyanurate groups corresponds to an NCO value of at least 5%, preferably at least 10%, more preferably at least 15% by weight (calculated as $C_3N_3O_3$ with a molar mass of 126 g/mol).

Examples of preferred polyisocyanates as component (A) include:

1) Polyisocyanates having isocyanurate groups and obtained from aromatic, aliphatic and/or cycloaliphatic diisocyanates. Particularly preferred here are the corresponding aliphatic and/or cycloaliphatic isocyanatoisocyanurates and in particular those based on hexamethylene diisocyanate and isophorone diisocyanate. The isocyanurates present are in particular trisisocyanatoalkyl or trisisocyanatocycloalkyl isocyanurates, which are cyclic trimers of the diisocyanates, or are mixtures with their higher homologs having more than one isocyanurate ring. The isocyanatoisocyanurates generally have an NCO content of from 10 to 30% by weight, in particular from 15 to 25% by weight, and an average NCO functionality of from 2.6 to 8.

2) Uretdione diisocyanates having aromatically, aliphatically and/or cycloaliphatically bonded isocyanate groups, preferably having aliphatically and/or cycloaliphatically bonded groups and in particular those derived from hexamethylene diisocyanate or isophorone diisocyanate. Uretdione diisocyanates are cyclic dimerization products of diisocyanates. The uretdione diisocyanates can be used as a sole component or as a mixture with other polyisocyanates, in particular those mentioned under 1).

3) Polyisocyanates having biuret groups and having aromatically, cycloaliphatically or aliphatically bonded, preferably cycloaliphatically or aliphatically bonded, isocyanate groups, in particular tris(6-isocyanatohexyl)biuret or mixtures thereof

with its higher homologs. These polyisocyanates having biuret groups generally have an NCO content of from 18 to 22% by weight and an average NCO functionality of from 2.8 to 6.

4) Polyisocyanates having urethane and/or allophanate groups and having aromatically, aliphatically or cycloaliphatically bonded, preferably aliphatically or cycloaliphatically bonded, isocyanate groups, as can be obtained, for example, by reaction of excess amounts of hexamethylene diisocyanate or of isophorone diisocyanate with mono- or polyhydric alcohols, such as, for example, methanol, ethanol, isopropanol, n-propanol, n-butanol, isobutanol, sec-butanol, tert-butanol, n-hexanol, n-heptanol, n-octanol, n-decanol, n-dodecanol (lauryl alcohol), 2 ethylhexanol, n-pentanol, stearyl alcohol, cetyl alcohol, lauryl alcohol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 1,3-propanediol monomethyl ether, cyclopentanol, cyclohexanol, cyclooctanol, cyclododecanol, trimethylolpropane, neopentyl glycol, pentaerythritol, 1,4-butanediol, 1,6 hexanediol, 1,3 propanediol, 2-ethyl-1,3-propanediol, 2-methyl-1,3-propanediol, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol, glycerol, 1,2-dihydroxypropane, 2,2-dimethyl-1,2-ethanediol, 1,2-butane-diol, 1,4-butanediol, 3-methylpentane-1,5-diol, 2-ethylhexane-1,3-diol, 2,4-diethyl-octane-1,3-diol, neopentyl glycol hydroxypivalate, ditrimethylolpropane, dipentaerythritol, 2,2-bis(4-hydroxycyclohexyl)propane, 1,1-, 1,2-, 1,3-, and 1,4 cyclohexanedimethanol, 1,2-, 1,3-, or 1,4-cyclohexanediol or mixtures thereof. These polyisocyanates having urethane and/or allophanate groups generally have an NCO content of from 12 to 24% by weight, in particular 18-24% by weight for those based on HDI, and an average NCO functionality of from 2.5 to 4.5.

5) Polyisocyanates comprising oxadiazinetrione groups, preferably derived from hexamethylene diisocyanate or isophorone diisocyanate. Such polyisocyanates comprising oxadiazinetrione groups can be prepared from diisocyanate and carbon dioxide.

6) Polyisocyanates comprising iminooxadiazinedione groups, preferably derived from hexamethylene diisocyanate or isophorone diisocyanate. Such polyisocyanates comprising iminooxadiazinedione groups can be prepared from diisocyanates by means of specific catalysts.

7) Uretonimine-modified polyisocyanates.

8) Carbodiimide-modified polyisocyanates.

9) Hyperbranched polyisocyanates, of the kind known for example from DE-A1 10013186 or DE-A1 10013187.

10) Polyurethane polyisocyanate prepolymers, from di- and/or polyisocyanates with alcohols.

11) Polyurea-polyisocyanate prepolymers.

The polyisocyanates 1) to 11) can be used as a mixture, if appropriate also as a mixture with diisocyanates.

Preference is given to polyisocyanates containing isocyanurate and/or biuret groups. In addition, these mixtures may also contain minor amounts of uretdione, biuret, urethane, allophanate, oxadiazinetrione, iminooxadiazinedione and/or uretonimine groups, preferably at less than 25% by weight in each case, more preferably less than 20% by weight in each case, very preferably less than 15% by weight in each case, in particular below 10% by weight in each case and especially below 5% by weight in each case, and very specially below 2% by weight in each case, based on the respective functional group.

Particularly preferred as isocyanates in component (A) are isocyanurates of isophorone diisocyanate having an NCO content according to DIN EN ISO 11909 of 16.7% – 17.6%, and/or an average NCO functionality of from 3.0 to 4.0, preferably from 3.0 to 3.7, more preferably from 3.1 to 3.5. Compounds of this kind containing isocyanurate groups preferably have a HAZEN/APHA color number according to DIN EN 1557 of not more than 150.

Also particularly preferred as isocyanate in component (A) is the isocyanurate of 1,6-hexamethylene diisocyanate, having an NCO content to DIN EN ISO 11909 of 21.5 – 23.5%, and/or an average NCO functionality of 3.0 to 8, preferably 3.0 to 3.7, more preferably 3.1 to 3.5. Compounds of this kind containing isocyanurate groups preferably have a color number to DIN ISO 6271 of not more than 60. Compounds of this kind containing isocyanurate groups preferably have a viscosity at 23°C to DIN EN ISO 3219 of 1000 to 20 000 mPas, preferably 1000 to 4000 mPas, at a shear rate of 1000 s^{-1}.

In one preferred embodiment the isocyanate component (A) has a total chlorine content of less than 400 mg/kg, more preferably a total chlorine content of less than 80 mg/kg, very preferably less than 60, in particular less than 40, especially less than 20, and less than 10 mg/kg even.

Binder component (B)

Binders suitable for the present invention are known to the person skilled in the art or can be synthesized according to methods known to the person skilled in the art.

A binder for the purpose of the present invention is a compound containing at least two hydrogen atoms reactive to isocyanates. Preferably, the binder contains hydroxyl groups (OH groups) and/or primary and/or secondary amino groups.

For the purpose of the present invention, a polyol is an organic molecule comprising an average number of at least 2 OH groups per molecule (number-weighted). Furthermore, a polyamine is an organic molecule comprising an average number of at least 2 primary or secondary (i.e., reactive) amino groups per molecule (number-weighted).

Preferably, the binder component (B) contains at least one polyol or at least one polyamine or both, at least one polyol and at least one polyamine. Particular preference is given to binder components (A) containing at least one polyol.

Component (B) preferably exhibits an OH number according to DIN 53240-2 of at least 15, preferably at least 40, more preferably at least 60, and very preferably at least 80 mg KOH/g resin solids. The OH number can be up to 350, preferably up to 240, more preferably up to 180, and very preferably up to 140 mg KOH/g resin solids.

The preferred OH numbers are also dependent on the application. According to Manfred Bock, "Polyurethane für Lacke und Beschichtungen", p. 80, Vincentz-Verlag, 1999, lower OH numbers are advantageous for effective adhesion and corrosion control. For topcoat materials, for example, use is made of polyacrylates having OH numbers of about 40 to 100; for weather-resistant coating materials, OH numbers of around 135; and for high chemical resistance, those with OH numbers of around 170 mg KOH/g resin solids are used. Polyesters for aircraft coatings have in some cases much higher OH numbers.

Examples of such preferred binders are polyacrylate polyols, polyester polyols, polyether polyols, polyurethane polyols; polyurea polyols; polyester polyacrylate polyols; polyester polyurethane polyols; polyurethane polyacrylate polyols, polyurethane-modified alkyd resins; fatty acid modified polyester polyurethane polyols, copolymers with allyl ethers, graft polymers of the stated groups of compound with, for example, different glass transition temperatures, and also mixtures of the binders stated. Particular preference is given to polyacrylate polyols, polyester polyols and polyether polyols, in particular to at least one polyacrylate polyol that contains per molecule on average at least two, preferably two to ten, more preferably three to ten, and very preferably three to eight hydroxyl groups.

Preferred OH numbers, measured in accordance with DIN 53240-2, are from 40 to 350 mg KOH/g resin solids for polyesters, preferably from 80 to 180 mg KOH/g resin solids, and from 15 to 250 mg KOH/g resin solids for polyacrylate-ols, preferably from 80 to 160 mg KOH/g.

The binders may additionally have an acid number according to DIN EN ISO 3682 of up to 200 mg KOH/g, preferably up to 150 and more preferably up to 100 mg KOH/g.

The acid number ought preferably to be at least 10, more preferably at least 80 mg KOH/g. Alternatively it may be less than 10, so that the binder is virtually acid-free.

Polyacrylate polyols of this kind preferably have a molecular weight Mn of at least 1000, more preferably at least 2000 and very preferably at least 5000 g/mol. The molecular weight Mn may for example be up to 200 000, preferably up to 100 000, more preferably up to 80 000 and very preferably up to 50 000 g/mol.

The polyacrylate polyols are copolymers of at least one (meth)acrylic ester with at least one compound having at least one, preferably precisely one hydroxy group and at least one, preferably precisely one (meth)acrylate group.

The latter may be, for example monoesters of α,β-unsaturated carboxylic acids, such as acrylic acid, methacrylic acid (referred to in this specification for short as “(meth)acrylic acid”), with diols or polyols, which have preferably 2 to 20 C atoms and at least two hydroxy groups, such as ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,1-dimethyl-1,2-ethanediol, dipropylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol, tripropylene glycol, 1,4-butanediol, 1,5-pentanediol, neopentyl glycol, neopentyl glycol hydroxypivalate, 2-ethyl-1,3-propanediol, 2-methyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, 1,6-hexanediol, 2-methyl-1,5-pentanediol, 2-ethyl-1,4-butanediol, 2-ethyl-1,3-hexanediol, 2,4-diethyl-octane-1,3-diol, 2,2-bis(4-hydroxycyclohexyl)propane, 1,1-, 1,2-, 1,3- and 1,4-bis(hydroxymethyl)cyclohexane, 1,2-, 1,3- or 1,4-cyclohexanediol, glycerol, trimethylolethane, trimethylolpropane, trimethylolbutane, pentaerythritol, ditrimethylolpropane, dipentaerythritol, sorbitol, mannitol, diglycerol, threitol, erythritol, adonitol (ribitol), arabitol (lyxitol), xylitol, dulcitol (galactitol), maltitol, isomalt, poly-THF with a molar weight between 162 and 4500, preferably 250 to 2000, poly-1,3-propanediol or polypropylene glycol with a molar weight between 134 and 2000 or polyethylene glycol with a molar weight between 238 and 2000.

Preference is given to 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2- or 3-hydroxypropyl acrylate, 1,4-butanediol monoacrylate or 3-(acryloyloxy)-2-hydroxypropyl acrylate and particular preference to 2-hydroxyethyl acrylate and/or 2-hydroxyethyl methacrylate.

The hydroxyl-bearing monomers are used in the copolymerization in a mixture with other polymerizable monomers, preferably free-radically polymerizable monomers, preferably those composed of more than 50% by weight of C_1–C_{20}, preferably C_1-C_4, alkyl (meth)acrylate, (meth)acrylic acid, vinylaromatics having up to 20 C atoms, vinyl esters of carboxylic acids comprising up to 20 C atoms, vinyl halides, nonaromatic hydrocarbons having 4 to 8 C atoms and 1 or 2 double bonds, unsaturated nitriles and mixtures thereof. Particular preference is given to those polymers composed of more than 60% by weight of C_1–C_{10} alkyl (meth)acrylates, styrene, vinylimidazole or mixtures thereof.

Above these the polymers may comprise hydroxy-functional monomers in accordance with the above hydroxy group content and, if appropriate, further monomers, examples being (meth)acrylic acid glycidyl epoxy esters, ethylenically unsaturated acids, especially carboxylic acids, acid anhydrides or acid amides.

Further polymers are, for example, polyesterols, as are obtainable by condensing polycarboxylic acids, especially dicarboxylic acids, with polyols, especially diols. In order to ensure a polyester polyol functionality that is appropriate for the polymerization, use is also made in part of triols, tetrols, etc, and also triacids etc.

Polyester polyols are known for example from Ullmanns Enzyklopädie der technischen Chemie, 4th edition, volume 19, pp. 62 to 65. It is preferred to use polyester polyols which are obtained by reacting dihydric alcohols with dibasic carboxylic acids. In lieu of the free polycarboxylic acids it is also possible to use the corresponding polycarboxylic anhydrides or corresponding polycarboxylic esters of lower alcohols or mixtures thereof to prepare the polyester polyols. The polycarboxylic acids may be aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic and may if appropriate be substituted, by halogen atoms for example, and/or unsaturated. Examples thereof that may be mentioned include the following:

Oxalic acid, maleic acid, fumaric acid, succinic acid, glutaric acid, adipic acid, sebacic acid, dodecanedioic acid, o–phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, azelaic acid, 1,4-cyclohexanedicarboxylic acid or tetrahydrophthalic acid, suberic acid, azelaic acid, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, tetrachlorophthalic anhydride, endomethylenetetrahydrophthalic anhydride, glutaric anhydride, maleic anhydride, dimeric fatty acids, their isomers and hydrogenation products, and also esterifiable derivatives, such as anhydrides or dialkyl esters, C_1 C_4 alkyl esters for example, preferably methyl, ethyl or n-butyl esters, of the stated acids are employed. Preference is given to dicarboxylic acids of the general formula

HOOC-(CH2)y-COOH, where y is a number from 1 to 20, preferably an even number from 2 to 20, and preferably succinic acid, adipic acid, sebacic acid, and dodecanedicarboxylic acid.

Suitable polyhydric alcohols for preparing the polyesterols include 1,2-propanediol, ethylene glycol, 2,2-dimethyl-1,2-ethanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 3-methylpentane-1,5-diol, 2-ethylhexane-1,3-diol, 2,4-diethyloctane-1,3-diol, 1,6-hexanediol, Poly-THF having a molar mass of between 162 and 4500, preferably 250 to 2000, poly-1,3-propanediol having a molar mass between 134 and 1178, poly-1,2-propanediol having a molar mass between 134 and 898, polyethylene glycol having a molar mass between 106 and 458, neopentyl glycol, neopentyl glycol hydroxypivalate, 2-ethyl-1,3-propanediol, 2-methyl-1,3-propanediol, 2,2-bis(4-hydroxycyclohexyl)propane, 1,1-, 1,2-, 1,3- and 1,4-cyclohexanedimethanol, 1,2-, 1,3- or 1,4-cyclohexanediol, trimethylolbutane, trimethylolpropane, trimethylolethane, neopentyl glycol, pentaerythritol, glycerol, ditrimethylolpropane, dipentaerythritol, sorbitol, mannitol, diglycerol, threitol, erythritol, adonitol (ribitol), arabitol (lyxitol), xylitol, dulcitol (galactitol), maltitol or isomalt, which if appropriate may have been alkoxylated as described above.

Preferred alcohols are those of the general formula $HO-(CH_2)_x-OH$, where x is a number from 1 to 20, preferably an even number from 2 to 20. Preferred are ethylene glycol, butane-1,4-diol, hexane-1,6-diol, octane-1,8-diol and dodecane-1,12-diol. Additionally preferred is neopentyl glycol.

Also suitable, furthermore, are polycarbonate diols of the kind obtainable, for example, by reacting phosgene with an excess of the low molecular mass alcohols specified as synthesis components for the polyester polyols.

Also suitable are lactone-based polyester diols, which are homopolymers or copolymers of lactones, preferably hydroxy-terminated adducts of lactones with suitable difunctional starter molecules. Suitable lactones are preferably those which derive from compounds of the general formula $HO-(CH_2)_z-COOH$, where z is a number from 1 to 20 and where one H atom of a methylene unit may also have been substituted by a C1 to a C4 alkyl radical. Examples are ε-caprolactone, β-propiolactone, gamma–butyrolactone and/or methyl-ε-caprolactone, 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid or pivalolactone, and mixtures thereof. Examples of suitable starter components include the low molecular mass dihydric alcohols specified above as a synthesis component for the polyester polyols. The corresponding polymers of ε-caprolactone are particularly preferred. Lower polyester diols or polyether diols as well can be used as starters for preparing the lactone polymers. In lieu of the polymers of lactones it is also possible to use the corresponding, chemically equivalent polycondensates of the hydroxycarboxylic acids corresponding to the lactones.

Also suitable as polymers, furthermore, are polyetherols, which are prepared by addition reaction of ethylene oxide, propylene oxide or butylene oxide with H–active components. Polycondensates of butanediol are also suitable.

In addition it is possible to use hydroxy-functional carboxylic acids, such as dimethylolpropionic acid or dimethylolbutanoic acid, for example.

The polymers can of course also be compounds containing primary or secondary amino groups.

Polyhedral oligomeric stannasilsesquioxane (C)

According to the invention, the curable composition comprises at least one polyhedral oligomeric silsesquioxane with the number of cages z per molecule being from 2 to 3 and the number of Sn atoms per molecule being at least one.

In a preferred embodiment, the composition comprises at least one polyhedral oligomeric silsesquioxanes which is a polyhedral oligomeric stannasilsesquioxane according to formula (I):

$$[(R^1SiO_{1,5})_m(R^2SiO)_n(SnO)_jX_p]_z(Y)_q \quad (I),$$

the symbols having the following meaning:

R^1 and R^2 may be the same or different and each represents a C_{6-30} aryl, C_{1-40} alkyl, C_{5-40} cycloalkyl, C_{7-14} aralkyl, or a siloxy radical.

Each of the before mentioned radicals R^1 and/or R^2 may optionally contain at least one functional group selected from amino, carbonyl, carboxyl, ester, hydroxyl, carbon-carbon double bond, ether group, F, Cl, Br, or I. In case R^1 and/or R^2 contain one ore more of the before mentioned functional groups, such radical is referred to as substituted radical.

Furthermore, some of the carbon atoms of the before mentioned radicals may optionally be replaced by heteroatoms, in particular nitrogen, oxygen, sulfur, phosphorus or silicon.

The radicals R^1 and/or R^2 may be present as branched or unbranched chains or as cyclic-hydrocarbon radicals. Examples of hydrocarbon radicals which can be used as R^1 or R^2 include, without the invention being restricted to these: methyl, ethyl, propyl, n-butyl, i-butyl, pentyl, hexyl, heptyl, octyl, nonyl, dodecanyl, benzyl, phenyl, cyclopropyl, cyclobutyl, cyclohexyl, cyclopentyl, cycloheptyl, cyclododecanyl or organosilicon radicals.

The above-mentioned hydrocarbon radicals can also represent a radical that has at least one multiple bond such as a double or triple bond, e.g. a propenyl, vinyl, cyclododecatrienyl, butenyl, butynyl or cyclopentenyl radical. The hydrocarbon radicals are usually bound to the silicon atom in the silasesquioxane via an Si-C bond.

The radicals R^1 and R^2 in these oligomeric silsesquioxanes are preferably selected from at least one radical of the following group: methyl, ethyl, propyl, butyl, i-butyl, cyclopropyl, cyclobutyl, cyclopentyl, cycloheptyl, cyclooctanyl, cyclononanyl, cyclodecanyl, vinyl, propenyl, monounsaturated or polyunsaturated butenyl, cyclopropenyl, monounsaturated or polyunsaturated cyclobutenyl, monounsaturated or polyunsaturated cyclopentenyl, monounsaturated or polyunsaturated cyclohexenyl, monounsaturated or polyunsaturated cycloheptenyl, monounsaturated or polyunsaturated cyclooctenyl, ethynyl, propynyl, monounsaturated or polyunsaturated butynyl, benzyl and/or pyridyl.

The term "polyunsaturated" as a prefix for butenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, cycloheptenyl, cyclooctenyl, and butynyl groups, thereby represents one or more additional double or triple bonds up to the theoretical maximum including also aromatic systems.

The radicals R^1 and/or R^2 may each be either substituted or unsubstituted. In principal, there are no restrictions concerning the nature of the substituent. Substituted radicals R^1 and/or R^2 may have, for example, a halogen atom such as chlorine or bromine in place of a hydrogen atom. The substitution of radical R^1 and R^2 may positively influence the dispersibility of the catalyst in a solvent and in the resulting coating.

In a particularly preferred embodiment, R^1 and R^2 independent from each other represent an aryl radical, in particular phenyl ($-C_6H_5$), or an alkyl radical, in particular cyclopentyl ($-C_5H_4$), octyl, hexyl, or iso-butyl.

The oligomeric silsesquioxanes of the invention particularly preferably have identical groups as radicals R ($R^1 = R^2$), particularly preferred R^1=R^2=aryl radical, in particular R^1=R^2=phenyl.

Y is a suitable anion. Y_q is chosen such that the polyhedral oligomeric silsesquioxane according to the present invention is not charged. For the purposes of the present invention, anionic radicals Y can be both, inorganic radicals such as halide ions, hydroxide ions or nitrate ions and organic radicals such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl or tert-butyl radicals, e.g. F^-, Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, OAc^-, OH^-. q represents an integer from 0 to 4. q is selected to make the compound according to formula (I) electrically neutral, i.e., q is dedicated to compensate potential charges.

X represents OH, F, Cl, Br, I, alkoxide, acetate, amine, peroxide, isocyanate, alkyl, aryl, O, or OR^1, wherein R^1 has the meaning as defined above.

j represents an integer from 1 to 3, preferably j = 1.

p represents an integer from 1 to 6, preferably 1.

z refers to the number of cages per molecule and represents an integer from 2 to 3. Particular preference is given to z = 3.

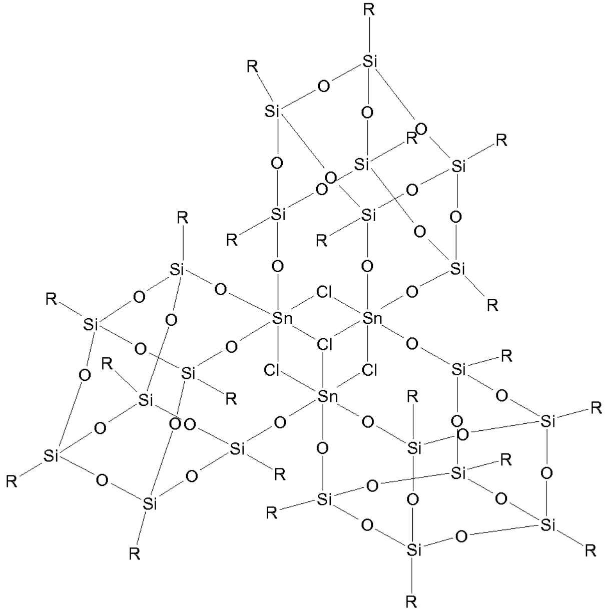
m represents an integer from 6 to 12, preferably 6.

n represents an integer from 0 to 4, preferably 1.

According to a particularly preferred embodiment, the integer m is 6, integer n is 1, integer j is 1 and integer p is 1.

Preferably, X represents an oxo group (i.e., X = monoatomic oxygen).

In a particularly preferred embodiment, the polyhedral oligomeric stannasilsesquioxane has a structure according to the following formula (II):



(II).

Preferably, the compositions according to this invention contain from 0.5 to 30 % by weight of component C) relative to the total weight of the composition.

Further components

Preferably, a curable composition according to the invention further comprises a solvent (D).

Examples of solvents (D) are alcohols, esters, ester alcohols, ethers, ether alcohols, aromatic and/or (cyclo)aliphatic hydrocarbons and their mixtures and halogenated hydrocarbons. Via the amino resins it is also possible to introduce alcohol as well into the mixtures.

Preference is given to alkanoic acid alkyl esters, alkanoic acid alkyl ester alcohols, alkoxylated alkanoic acid alkyl esters and mixtures thereof.

Examples of esters include n-butyl acetate, ethyl acetate, 1-methoxyprop-2-yl acetate and 2-methoxyethyl acetate, and also the monoacetyl and diacetyl esters of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol or tripropylene glycol, such as butyl glycol acetate, for example. Further examples are carbonates, as well, such as preferably 1,2-ethylene carbonate, 1,2-propylene carbonate or 1,3-propylene carbonate.

Ethers are, for example, tetrahydrofuran (THF), dioxane, and the dimethyl, diethyl or di-n butyl ethers of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol or tripropylene glycol.

Alcohols are for example methanol, ethanol, isopropanol, n-propanol, n-butanol, isobutanol, sec-butanol, n-hexanol, n-heptanol, n-octanol, n-decanol, n-dodecanol (lauryl alcohol), 2-ethylhexanol, cyclopentanol or cyclohexanol.

Alkanoic ester alcohols are for example poly(C_2 to C_3) alkylene glycol (C_1 to C_4) monoalkyl ether acetates.

Ether alcohols are for example poly(C_2 to C_3) alkylene glycol di(C_1 to C_4) alkyl ethers, dipropylene glycol dimethyl ether, preferably butyl glycol.

Aromatic hydrocarbon mixtures are those comprising predominantly aromatic C_7 to C_{14} hydrocarbons and being able to comprise a boiling range from 110 to 300°C, particular preference being given to toluene, o-, m- or p-xylene, trimethylbenzene isomers, tetramethylbenzene isomers, ethylbenzene, cumene, tetrahydronaphthalene and mixtures comprising them.

Examples thereof are the Solvesso® grades from ExxonMobil Chemical, especially Solvesso® 100 (CAS no. 64742-95-6, predominantly C9 and C10 aromatics, boiling range about 154 – 178°C), 150 (boiling range about 182 – 207°C) and 200 (CAS no. 64742-94-5), and also the Shellsol® grades from Shell, Caromax® grades from Petrochem Carless, Caromax® 18, for example, or products from DHC, Hydrosol® A/170, for example. Hydrocarbon mixtures comprising paraffins, cycloparaffins and aromatics are also available commercially under the names Kristalloel (for example, Kristalloel 30, boiling range about 158 - 198°C or Kristalloel 60: CAS no. 64742-82-1), white spirit (likewise, for example CAS no. 64742-82-1) or solvent naphtha (light: boiling range about 155 – 180°C, heavy: boiling range about 225 – 300°C). The aromatics content of such hydrocarbon mixtures is generally more than 90%, preferably more than 95%, more preferably more than 98% and very preferably more than 99% by weight. It may be advisable to use hydrocarbon mixtures having a particularly reduced naphthalene content.

The density at 20°C to DIN 51757 of the hydrocarbons may be less than 1 g/cm^3, preferably less than 0.95 and more preferably less than 0.9 g/cm^3.

The aliphatic hydrocarbon content is generally less than 5%, preferably less than 2.5% and more preferably less than 1% by weight.

Halogenated hydrocarbons are, for example chlorobenzene and dichlorobenzene or its isomer mixtures.

(Cyclo)aliphatic hydrocarbons are for example decalin, alkylated decalin, and isomer mixtures of linear or branched alkanes and/or cycloalkanes.

Preference is given to n-butyl acetate, ethyl acetate, 1-methoxyprop-2-yl acetate, 2-methoxyethyl acetate, and mixtures thereof.

Mixtures of this kind can be produced in a volume ratio 10:1 to 1:10, preferably in a volume ratio of 5:1 to 1:5 and more preferably in a volume ratio of 1:1, not counting any solvent still comprised in the reaction mixture from the transetherification, and particularly not the alcohols R_1OH and R_2OH.

Preferred examples are butyl acetate/xylene, 1:1 methoxypropyl acetate/xylene, 1:1 butyl acetate/solvent naphtha 100, 1:2 butyl acetate/Solvesso® 100, and 3:1 Kristalloel 30/Shellsol® A.

Alcohols are for example methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, isobutanol, pentanol isomer mixtures, hexanol isomer mixtures, 2-ethylhexanol or octanol.

Examples of further, typical coatings additives (E) that can be used include antioxidants, stabilizers, activators (accelerants), fillers, pigments, dyes, antistats, flame retardants, thickeners, thixotropic agents, surface-active agents, viscosity modifiers, plasticizers or chelating agents.

Suitable thickeners, besides free-radically (co)polymerized (co)polymers, include typical organic and inorganic thickeners such as hydroxymethylcellulose or bentonite.

Examples of chelating agents that can be used include ethylenediamineacetic acid and its salts, and β-diketones.

Suitable fillers comprise silicates, examples being silicates obtainable by silicon tetrachloride hydrolysis, such as Aerosil® from Degussa, siliceous earth, talc, aluminum silicates, magnesium silicates, calcium carbonates, etc.

Suitable stabilizers comprise typical UV absorbers such as oxanilides, triazines and benzotriazole (the latter available as Tinuvin® grades from Ciba-Spezialitätenchemie) and benzophenones. They can be used alone or together with suitable free-radical scavengers, examples being sterically hindered amines such as 2,2,6,6-tetramethylpiperidine, 2,6-di-tert-butylpiperidine or derivates thereof, e.g., bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate. Stabilizers are used typically in amounts of 0.1% to 5.0% by weight, based on the solid components comprised in the preparation.

Pigments may likewise be comprised. Pigments, according to CD Römpp Chemie Lexikon – Version 1.0, Stuttgart/New York: Georg Thieme Verlag 1995, with reference to DIN 55943, are particulate, organic or inorganic chromatic or achromatic colorants which are virtually insoluble in the application medium.

Virtually insoluble here means a solubility at 25°C of below 1 g/1000 g of application medium, preferably below 0.5, more preferably below 0.25, very preferably below 0.1 and in particular below 0.05 g/1000 g of application medium.

Examples of pigments comprise any desired systems of absorption pigments and/or effect pigments, preferably absorption pigments. There are no restrictions concerning the number and selection of the pigment components. They can be adapted as desired to the particular requirements, such as the desired color impression, for example.

By effect pigments are meant all pigments which exhibit a platelet-shaped construction and impart specific decorative color effects to a surface coating. The effect pigments comprise, for example, all of the effect-imparting pigments which can be employed commonly in vehicle finishing and industrial coating. Examples of effect pigments of this kind are pure metal pigments, such as aluminum, iron or copper pigments; interference pigments, such as titanium dioxide-coated mica, iron oxide-coated mica, mixed oxide-coated mica (e.g., with titanium dioxide and Fe_2O_3 or titanium dioxide and Cr_2O_3), metal oxide-coated aluminum, or liquid-crystal pigments.

The color-imparting absorption pigments are, for example, typical organic or inorganic absorption pigments which can be used in the coatings industry. Examples of organic absorption pigments are azo pigments, phthalocyanine pigments, quinacridone pigments and pyrrolopyrrole pigments. Examples of inorganic absorption pigments are iron oxide pigments, titanium dioxide and carbon black.

The solids content of the coating compositions of the invention is laid down for the purposes of this specification as the ratio of the sum of the components (A), (B) and (C) to the sum of components (A), (B), (C) and (D). In accordance with the invention, said solids content is for example between 25% and 90% by weight, preferably between 40% and 80% by weight.

The components (A) and (B) are typically employed in a ratio of 0.2 : 1 to 5 : 1 (based on the ratio of the NCO groups in (A) to OH groups in (B)), preferably in the ratio of 0.4 : 1 to 3:1, more preferably in the ratio of 0.5 : 1 to 2 : 1, and very preferably in the ratio of 0.8 : 1 to 1.2 : 1.

Applications

The curable compositions of this invention are useful as coatings and may in particular be utilized as primers, topcoats or as clearcoats and/or basecoats in cleacoat/basecoat compositions. They are also useful in spray applications.

The curable compositions lead to fast reacting, durable coatings having extended pot-life and excellent cure. The curable compositions of the present invention provide a clearcoat having improved scratch resistance. The compositions of this invention can in principle also be utilized as adhesives, elastomers and plastics.

The coating materials of the invention are suitable for coating substrates including wood, paper, textile, leather, non-wovens, plastics surfaces, glass, ceramic, mineral building materials such as cement moldings and fiber-cement slabs, coated or uncoated metals. Preference is given to the use of the curable compositions for the coating of plastics or metals, particularly in the form of sheets, more preferably to the coating of surfaces made of metal.

The coating materials of the invention are suitable as interior coatings or in interior coatings, and also – this is preferred - as or in exterior coatings, i.e., applications where they are exposed to daylight, on parts of buildings, coatings on vehicles and aircraft, and for industrial applications. In particular the coating materials of the invention are used as or in automotive clearcoat, basecoat and topcoat materials or primers. Further preferred applications are the use for can coatings and coil coatings.

They are particularly suitable for use as primers, surfacers, pigmented topcoat materials and clearcoat materials in the sectors of industrial, wood, automotive, especially OEM, finishing or decorative coating. The coating compositions are especially suitable for applications where there is a need for particularly high application reliability, external weathering resistance, optical qualities, scratch resistance, solvent resistance and/or chemical resistance.

The substrates are coated with the coating materials of the invention in accordance with conventional techniques which are known to the skilled worker, and which involve applying at least one coating material or coating formulation of the invention to the target substrate in the desired thickness, and removing the volatile constituents of the coating material with heating if appropriate (drying). This operation may, if desired, be repeated one or more times. Application to the substrate may be made in a known way, for example by spraying, troweling, knife coating, brushing, rolling, roller-coating or pouring. The coating thickness is generally in a range from about 3 to 1000 g/m2 and preferably 10 to 200 g/m^2. Curing may then be carried out.

Curing is generally accomplished by drying the coatings - following application of the coating material to the substrates - at a temperature if appropriate below 80°C, preferably room temperature to 60°C and more preferably room temperature to 40°C, over a period of up to 72 hours, preferably up to 48 hours, more preferably up to 24 hours, very preferably up to 12 hours and in particular up to 6 hours, and subjecting the applied coatings to thermal treatment (curing) under an oxygen-containing atmosphere, preferably air or under inert gas, at temperatures between 80 and 270, preferably between 100 and 240 and, more preferably between 120 and 180°C. Curing of the coating material takes place as a function of the amount of coating material applied and of the crosslinking energy introduced via high-energy radiation, heat transfer from heated surfaces, or via convection of gaseous media, over a period of seconds, for example, in the case of coil coating in combination with NIR drying, up to 5 hours, for example, high-build systems on temperature sensitive materials, usually not less than 10 minutes, preferably not less than 15, more preferably not less than 30, and very preferably not less than 45 minutes. Drying essentially comprises removal of existing solvent, and in addition there may also, even at this stage, be reaction with the binder, whereas curing essentially comprises reaction with the binder.

In addition to or instead of thermal curing, the curing may also take place by means of IR and NIR radiation, with NIR radiation here denoting electromagnetic radiation in the wavelength range from 760 nm to 2.5 µm, preferably from 900 to 1500 nm.

Curing takes place in a time of 1 second to 60 minutes, preferably of 1 minute to 45 minutes.

Examples of suitable substrates for the coating materials of the invention include thermoplastic polymers, especially polymethyl methacrylates, polybutyl methacrylates, polyethylene terephthalates, polybutylene terephthalates, polyvinylidene fluorides, polyvinyl chlorides, polyesters, polyolefins, acrylonitrile-ethylenepropylene-diene-styrene copolymers (A–EPDM), polyetherimides, polyether ketones, polyphenylene sulfides, polyphenylene ethers or mixtures thereof.

Mention may further be made of polyethylene, polypropylene, polystyrene, polybutadiene, polyesters, polyamides, polyethers, polycarbonate, polyvinylacetal, polyacrylonitrile, polyacetal, polyvinyl alcohol, polyvinyl acetate, phenolic resins, urea resins, melamine resins, alkyd resins, epoxy resins or polyurethanes, block or graft copolymers thereof, and blends of these.

Mention may preferably be made of ABS, AES, AMMA, ASA, EP, EPS, EVA, EVAL, HDPE, LDPE, MABS, MBS, MF, PA, PA6, PA66, PAN, PB, PBT, PBTP, PC, PE, PEC, PEEK, PEI, PEK, PEP, PES, PET, PETP, PF, PI, PIB, PMMA, POM, PP, PPS, PS, PSU, PUR, PVAC, PVAL, PVC, PVDC, PVP, SAN, SB, SMS, UF, UP plastics (abbreviated names in accordance with DIN 7728) and aliphatic polyketones.

Particularly preferred substrates are polyolefins, such as PP (polypropylene), which optionally may be isotactic, syndiotactic or atactic and optionally may be unoriented or may have been oriented by uniaxial or biaxial stretching, SAN (styrene-acrylonitrile-copolymers), PC (polycarbonates), PVC (polyvinyl chlorides), PMMA (polymethyl methacrylates), PBT (poly(butylene terephthalate)s), PA (polyamides), ASA (acrylonitrile-styrene-acrylate copolymers) and ABS (acrylonitrile-butadiene-styrene-copolymers), and also their physical mixtures (blends). Particular preferably is given to PP, SAN, ABS, ASA and blends of ABS or ASA with PA or PBT or PC. Especially preferred are polyolefins, PMMA and PVC.

Especially preferred is ASA, particularly in accordance with DE 196 51 350 and the ASA/PC blend. Preference is likewise given to polymethyl methacrylate (PMMA) or impact-modified PMMA.

A further-preferred substrate for coating with the coating materials of the invention are metals. The metals in question are especially those which have already been coated with another coating film, such as with an electrocoat, surfacer, primer or basecoat. These coating films may be solvent-based, water-based or powder coating-based, may be crosslinked, part-crosslinked or thermoplastic, may have been cured through their volume or may have been applied wet-on-wet.

As far as the type of metal is concerned, suitable metals may in principle be any desired metals. In particular, however, they are metals or alloys which are typically employed as metallic materials of construction and require protection against corrosion.

The surfaces in question are in particular those of iron, steel, Zn, Zn alloys, Al or Al alloys. These may be the surfaces of structures composed entirely of the metals or alloys in question. Alternatively the structures may have been only coated with these metals and may themselves be composed of materials of other kinds, such as of other metals, alloys, polymers or composite materials, for example. They may be surfaces of castings made from galvanized iron or steel. In one preferred embodiment of the present invention the surfaces are steel surfaces.

Zn alloys or Al alloys are known to the skilled worker. The skilled worker selects the nature and amount of alloying constituents in accordance with the desired end-use application. Typical constituents of zinc alloys comprise, in particular, Al, Pb, Si, Mg, Sn, Cu or Cd. Typical constituents of aluminum alloys comprise, in particular, Mg, Mn, Si, Zn, Cr, Zr, Cu or Ti. The alloys may also be Al/Zn alloys in which Al and Zn are present in an approximately equal amount. Steel coated with alloys of these kinds is available commercially. The steel may comprise the typical alloying components known to the skilled worker.

Also conceivable is the use of the coating compositions of the invention for treating tin-plated iron/steel (tinplate).

The coatings obtainable from the curable compositions according to the invention exhibit an excellent scratch resistance. They can be produced by taking advantage of a high catalytic activity of component C) without containing any metal-organic or amine components.

P. Betz and A. Bartelt, Progress in Organic Coatings, 22 (1993), pages 27-37, discloses various methods of determining the scratch resistance of coatings.

The scratch resistance of the cured coatings is preferably assessed as follows with the aid of the BASF brush test as described in Fig. 2 on page 28 of the article by P. Betz and A. Bartelt, Progress in organic Coatings, 22 (1993), pages 27-37.

In this technique, the film surface is damaged using a weighted mesh fabric. The mesh fabric and the film surface are wetted generously with a detergent solution. The test panel is moved forward and backward in reciprocal movements under the mesh fabric by means of a motor drive.

The test panels may be produced according to the following procedure: an electrodeposition coating material is applied first of all in a film thickness of 18-22 micrometers, then a surfacer in a film thickness of 35-40 micrometers, then a black basecoat in a film thickness of 20-25 micrometers and, finally, the test coating composition in a film thickness of 40-45 micrometers, each of the films being cured. Following application of the coating materials, the panels are stored at room temperature for at least 2 weeks before the test is conducted.

The test element preferably is an eraser (4.5 x 2.0 cm, broad side perpendicular to the direction of scratching) lined with nylon mesh fabric (No. 11, 31 micrometer mesh size, Tg 50°C). The applied weight preferably is 2000 g.

The testing may take place according to the following procedure (BASF brush test): Prior to each test, the mesh fabric is replaced, with the running direction of the fabric meshes parallel to the direction of scratching. Using a pipette, about 1 ml of a freshly stirred 0.25% strength Persil solution is applied before the eraser. The rotational speed of the motor is set so that 80 double strokes are performed in a period of 80 s. After the test, the remaining washing liquid is rinsed off with cold tap water and the test panel is blown dry using compressed air. A measurement is made of the gloss in accordance with DIN 67530 before and after damage (direction of measurement perpendicular to the direction of scratching).

The coating compositions of the invention exhibit a markedly improved scratch resistance. Preferably, the coating composition of the invention in the cured state has a scratch resistance such that the delta gloss value following the BASF brush test of the cured coating composition applied over a basecoat is not more than 8, preferably not more than 4 and, with particular preference, is 0.

The examples which follow are intended to illustrate the properties of the invention, but without restriction thereof.

Examples

Preparation of Tin-POSS hybrid catalyst

Example 1: Single cage catalyst $[(C_6H_5)_7Si_7O_{11}(OH)Sn(acac)_2]_1$

2.5g of phenyltrisilanol POSS $[(C_6H_5)_7Si_7O_9(OH)_3]$ obtained from Hybrid Plastics and 1.1g of $Cl_2Sn(acac)_2$ was added to toluene (100 ml) and stirred well. Then triethylamine

(4 ml) was added into it and heated to 80°C overnight. The product mixture was a white dispersion, which was filtered and the filtrate was rotary evaporated completely with hexane to obtain crystals of tin containing POSS with z = 1.

Example 2: Three cage catalyst $\{[(C_6H_5)_7Si_7O_{12}Sn]_3(Cl)_4\}$

3.5 ml triethylamine was added to 50 ml toluene solution containing 5.0 g of phenyltrisilanol POSS $[(C_6H_5)_7Si_7O_9(OH)_3]$ obtained from Hybrid Plastics. The mixture was cooled down to 0°C. Then 1.50g of tin(IV)chloride in toluene (50 ml) was added drop wise to the phenyltrisilanol POSS solution under strong stirring. Then the reaction mixture was allowed to come to room temperature and stirred overnight. The product mixture was typically a white dispersion, which was filtered and the filtrate was rotary evaporated completely with hexane to obtain crystals of tin containing POSS with z = 3.

Preparation of coatings

Polyurethane coatings were prepared using Lupranol 1301 (trifunctional polyether polyol by BASF with solely secondary OH groups and an OH number according to DIN 53240 of 398 mg KOH/g and a viscosity at 25°C of 640 mPa.s according to DIN 51550) as binder component B) and Basonat HI 100 (polyisocyanate based on isocyanurated hexamethylene diisocyanate by BASF with an NCO content of 21.5 to 22.5 wt.-% according to DIN EN ISO 11909 and a viscosity at 23°C of 2500 to 4000 mPa.s at shear rate D = 1000 s^{-1} according to DIN EN ISO 3219) as isocyanate component A). To that end, 0.43g of catalyst (according to Ex. 1 and Ex. 2) was completely dispersed in butyl acetate (1 ml). Subsequently 1.75g of Lupranol 1301 and 2.374g of Basonat HI 100 was added to the catalyst dispersion and stirred strongly for 20 minutes. Then the curable coating compositions were applied to a commercially available Polyethylene terephthalate (PET) sheet using a coil bar coater and kept for drying at 60°C for 12 hours.

Table 1: Performance of the polyurethane coatings prepared by using different catalysts

Catalyst	dibutyltin dilaurate	According to example 1	According to example 2
Catalytic activity (rate of reaction) 1)	Very fast	Fast	Fast
Scratch Resistance 2)	Poor	Good	Very Good

[1] For the measurement of the catalytic activity, 0.1 g of Sn-POSS according to Ex. 1 or Ex. 2 or 0.1 g of dibutyltin dilaurate was mixed with 1 ml of butyl acetate, 1 mole of hexamethylene diisocyanate and 1 mole of 1,5-pentadiol. The resulting mixture was mixed strongly and coated on a thin PET sheet. The disappearance of the isocyanate peak at 2275cm^{-1} was observed at different intervals of time with an IR spectrometer.
Reaction Rate:
Very fast: Reaction occurs almost instantaneously
Fast: Reaction occurs instantaneously, but relatively slowly in the beginning

[2] The coatings were subjected to the same number of scratches obtained with a rough sponge which was applied with the same force on the coating substrate. Scratch Resistance:
Poor: Clearly scratches with dense lines are visible on the coating.
Good: Scratches/lines are visible on the coating, but the density and size of the lines is lower.
Very Good: Very few scratches/lines are visible on the coating.

Pencil Hardness Tests

A standard test method of film hardness by pencil (ASTM D3363-05) was done on the coatings. A Berol Turquoise pencil was used for the test. Polyurethane coatings were prepared using Lupranol 1301 as binder component B) and Basonat HI 100 as isocyanate component A). To that end, 0.45g (10 wt.-% based on polyurethane) or 0.21g (5 wt.-% based on polyurethane) of catalyst (according to Ex. 1 and Ex. 2) was completely dispersed in butyl acetate (2ml). Subsequently 1.75g of Lupranol 1301 and 2.374g of Basonat HI 100 was added to the catalyst dispersion and stirred strongly for 20 minutes. Then the curable coating composition was applied to a commercially available polycarbonate sheet using a coil bar coater and kept for drying at 60°C for 12 hours. The results of the pencil hardness test are given in Table 2.

Table 2.

Sample	Pencil Scratch Hardness (5 wt.-%)	Pencil Scratch Hardness (10 wt.-%)
Example 1	B	B
Example 2	4B	4B

Claims

1. A curable composition comprising the following components:
   A) at least one isocyanate,
   B) at least one binder, and
   C) at least one polyhedral oligomeric silsesquioxane, with the number of cages z per molecule being 2 or 3 and the number of tin atoms per molecule being at least one.

2. A curable composition according to claim 1, wherein the at least one polyhedral oligomeric silsesquioxane is a polyhedral oligomeric stannasilsesquioxane according formula (I)

$$[(R^1SiO_{1,5})_m(R^2SiO)_n(SnO)_jX_p]_z(Y)_q \qquad (I),$$

wherein

R¹ and R² may be the same or different and each represents a C_6-C_{30} aryl, C_1–C_{40} alkyl, C_5–C_{40} cycloalkyl, or siloxy group, wherein R^1 and/or R^2 optionally contain at least one functional group;

Y is a suitable anion;

X is selected from OH, F, Cl, Br, I, alkoxide, acetate, amine, peroxide, isocyanate, alkyl, aryl, monoatomic oxygen, or OR^1, wherein R^1 has the meaning as defined above;

j is an integer from 1 to 3,

p is an integer from 1 to 6,

z is an integer from 1 to 3,

q is an integer from 0 to 4,

m is an integer from 6 to 12, and

n is an integer from 0 to 4.

3. A curable composition according to claims 1 or 2, wherein said at least one binder is a polyol.

4. A curable composition according to claims 1 to 3, wherein said at least one isocyanate is a polyisocyanate.

5. A curable composition according to claims 1 to 4, wherein z is 3.

6. A curable composition according to claims 2 to 5, wherein j is 1.

7. A curable composition according to claims 1 to 6, wherein m is 6, n is 1, j is 1, and p is 1.

8. A curable composition according to claims 1 to 7, wherein X is monoatomic oxygen.

9. A curable composition according to claims 1 to 8, wherein the composition contains from 0.5 to 30 % by weight of component C) relative to the total weight of the coating composition.

10. A kit of parts for joint application, comprising as separate parts components A), B), and C) or a kit of parts comprising component B) as one separate part and a mixture of A) and C) as a second separate part or a kit of parts comprising component A) as a first separate part and a mixture of B) and C) as a second separate part, wherein A), B) and C) have the meaning as defined in any of claims 1 to 9.

11. Use of a polyhedral oligomeric silsesquioxanes as defined in any of claims 1 to 8 in coatings, lacquers, paintings, films or polymer compositions.

12. Coating obtainable by curing of a composition according to any of claims 1 to 9.

13. Use of polyhedral oligomeric silsesquioxanes containing at least one metal atom to increase the scratch resistance of coatings.

14. Use of a polyhedral oligomeric stannasilsesquioxane to increase the scratch resistance of polyurethane based coatings.

15. Use of polyhedral oligomeric silsesquioxanes as defined in any of claims 1 to 8 to increase the scratch-resistance of coatings.