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(54) Title: NON-AQUEOUS, LIQUID COATING COMPOSITIONS CURABLE BY FREE-RADICAL POLYMERIZATION OF OLEFINIC DOUBLE BONDS

(57) Abstract: Non-aqueous, liquid coating compositions curable by free-radical polymerization of olefinic double bonds with a resin solids content consisting of 50 to 100 wt.% of a binder solids content curable by free-radical polymerization of olefinic double bonds, 0 to 30 wt.% of at least one crosslinking agent C and 0 to 50 wt.% of at least one component D, wherein the weight percentages add up to 100 wt.%, wherein the binder solids content consists of 40 to 95 wt.% of at least one component A curable by free-radical polymerization of olefinic double bonds and 5 to 60 wt.% of at least one binder B curable by free-radical polymerization of olefinic double bonds, wherein the weight percentages of the at least one component A and the at least one binder B add up to 100 wt.%, wherein the at least one component A is liquid and/or is present in dissolved form and wherein the at least one binder B is present as particles of resin having a melting temperature of 60 to 160°C.

WO 2006/084182 A1

Title

Non-Aqueous, Liquid Coating Compositions Curable by Free-Radical Polymerization of Olefinic Double Bonds

Field of the Invention

The invention relates to novel non-aqueous, liquid coating compositions curable by free-radical polymerization of olefinic double bonds.

Description of the Prior Art

Non-aqueous, liquid coating compositions curable by free-radical polymerization of olefinic double bonds are known per se. The only examples, which will be mentioned here, are those UV-curable clear coating compositions known for use as automotive clear coats, such as those known, for example, from EP-A-0 540 884, WO 01/24946, U.S. 5,425,970 and U.S. 6,261,645.

It has now been found that the per se known non-aqueous, liquid coating compositions curable by free-radical polymerization of olefinic double bonds may be improved if they additionally contain, apart from the hitherto conventional components curable by free-radical polymerization of olefinic double bonds, a specific kind of binder curable by free-radical polymerization of olefinic double bonds. In this way, it is, for example, possible to achieve a higher solids content of the coating composition at an identical or slightly higher application viscosity, improved sagging properties at elevated temperatures and favorable solvent-attack properties towards previously applied coating layers. Solvent-attack properties are here to be viewed in the light of the level of the solids content in question.

Summary of the Invention

The invention is directed to non-aqueous, liquid coating compositions curable by free-radical polymerization of olefinic double bonds with a resin solids content consisting of 50 to 100 wt.% of a binder solids content curable by free-radical polymerization of olefinic double bonds, 0 to 30 wt.% of one or more crosslinking agents C and 0 to 50 wt.% of one or more components D,

wherein the weight percentages add up to 100 wt.%, wherein the binder solids content consists of 40 to 95 wt.% of one or more components A curable by free-radical polymerization of olefinic double bonds and 5 to 60 wt.% of one or more binders B curable by free-radical polymerization of olefinic double bonds, wherein the weight percentages of the at least one component A and the at least one binder B add up to 100 wt.%, wherein the at least one component A is liquid and/or is present in dissolved form and wherein the at least one binder B is present as particles of resin having a melting temperature of 60 to 160°C.

Detailed Description of the Embodiments

The coating compositions according to the invention are liquid and have a solids content of, for example, 40 to 100 wt.%, preferably of 45 to 85 wt.%. The application viscosities of the coating compositions are in the range of, for example, 20 to 40 seconds (determined as flow time according to DIN EN ISO 2431, DIN 4 cup, 20°C). The solids content of the coating compositions according to the invention is in each instance higher than that of a corresponding, comparable coating composition which does not, however, contain binder(s) B at an application viscosity which is in both cases adjusted to the same value. The optical quality (appearance) of a coating applied and cured from a coating composition according to the invention is often also better than in the case of a coating applied from a corresponding, comparable coating composition which does not, however contain binder(s) B.

The solids content of the coating compositions according to the invention consists of the resin solids content and the following optional components: pigments, fillers (extenders) and non-volatile additives.

The resin solids content of the coating compositions according to the invention consists of 50 to 100, preferably 70 to 100 wt.% of the binder solids content consisting of components A and B, 0 to 30 wt.% of one or more crosslinking agents C and 0 to 50 wt.% of one or more components D, wherein the weight percentages add up to 100 wt.%.

The binder solids content consists of 40 to 95 wt.%, preferably 50 to 95 wt.%, of one or more components A curable by free-radical polymerization of olefinic double bonds and 5 to 60 wt.%, preferably 5 to 50 wt.%, of one or more binders B curable by free-radical polymerization of olefinic double bonds.

The components A are conventional binders A1 and/or reactive diluents A2, in each case having free-radically polymerizable olefinic double bonds and in each case being liquid and/or soluble in an organic solvent (mixture), i.e., if the coating compositions contain organic solvent(s), the components A are present in the coating compositions in dissolved form.

Suitable binders A1 with free-radically polymerizable olefinic double bonds, which may be considered are, for example, conventional binders known to the person skilled in the art which can be crosslinked by free-radical polymerization. These binders are prepolymers, such as, polymers and oligomers containing, per molecule, one or more, preferably on average 2 to 20, particularly preferably 3 to 10 free-radically polymerizable olefinic double bonds. The polymerizable double bonds may, for example, be present in the form of (meth)acryloyl, vinyl, allyl, maleate and/or fumarate groups. The free-radically polymerizable double bonds are particularly preferably present in the form of (meth)acryloyl groups. Examples of such prepolymers are in particular (meth)acryloyl-functional (meth)acrylic copolymers, polyurethane (meth)acrylates, polyester (meth)acrylates, unsaturated polyesters, polyether (meth)acrylates, silicone (meth)acrylates and epoxy resin (meth)acrylates. The number average molar mass Mn of these compounds may, for example, be from 500 to 10,000 g/mol, preferably from 500 to 5000 g/mol. The binders A1 may be used individually or in combination.

Apart from the free-radically polymerizable olefinic double bonds, the binders A1 may also contain further functional, in particular crosslinkable, functional groups. Members of the resultant subgroup of binders A1 are denoted in the remainder of the description and in the claims as binders A1'. The binders A1' may be present in the coating compositions in combination with binders A1 containing no further crosslinkable functional groups. The further crosslinkable functional groups are in particular functional groups crosslinkable by condensation or addition reactions. Examples which may in particular be mentioned in this connection are hydroxyl groups. If the coating compositions contain binders A1', they generally also contain at least one crosslinking agent C with functional groups complementary to the crosslinkable groups of the binders A1'. For example, coating compositions containing binders A1' comprising hydroxyl groups may contain as crosslinking agent(s) C conventional crosslinking agents known to the person skilled in the art for coating systems based on OH-functional binders, for example, transesterification crosslinking agents; free or blocked polyisocyanate crosslinking agents; amino resin crosslinking agents, such as, melamine-formaldehyde resins; and/or trisalkoxycarbonyl aminotriazine crosslinking agents.

When binders A1 are mentioned in this description and in the claims, binders of the subgroup A1' are of course also included, except that the meaning is obviously limited to those binders A1 which, apart from the free-radically polymerizable olefinic double bonds, contain no further functional groups, in particular no crosslinkable functional groups.

The reactive diluents A2 are free-radically polymerizable low molecular weight compounds with a molar mass below 500 g/mol. The reactive diluents A2 may be mono-, di- or polyunsaturated. Examples of monounsaturated reactive diluents A2 are (meth)acrylic acid and the (cyclo)alkyl esters thereof, maleic acid and the semi-esters thereof, vinyl acetate, vinyl ethers, substituted vinyl ureas, styrene, vinyltoluene. Examples of diunsaturated reactive diluents A2 are di(meth)acrylates, such as, polyethylene glycol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, vinyl (meth)acrylate, allyl (meth)acrylate, divinylbenzene, dipropylene glycol di(meth)acrylate, hexanediol di(meth)acrylate. Examples of polyunsaturated reactive diluents A2 are glycerol tri(meth)acrylate, trimethylolpropane tri(meth)acrylate. The reactive diluents A2 may be used individually or in combination.

Like the binders A1 in the form of representatives of subgroup A1', the reactive diluents A2 may also contain, apart from the free-radically polymerizable olefinic double bonds, further thermally crosslinkable functional groups. Members of the resultant subgroup of reactive diluents A2 are denoted in the remainder of the description and in the claims as reactive diluents A2'. The reactive diluents A2' may be present in the coating compositions in combination with reactive diluents A2 containing no further crosslinkable functional groups. The further crosslinkable functional groups are in particular functional groups crosslinkable by condensation or addition reactions. Examples, which may in particular be mentioned in this connection, are hydroxyl groups. If the coating compositions contain reactive diluents A2', they generally also contain at least one crosslinking agent C with functional groups complementary to the crosslinkable groups of the reactive diluents A2'. For example, coating compositions containing reactive diluents A2' comprising hydroxyl groups may contain as crosslinking agent C conventional crosslinking agents known to the person skilled in the art for coating systems based on OH-functional binders, for example, those crosslinking agents already mentioned in relation to the description of the binders A1'. Examples of reactive diluents A2' with hydroxyl groups are compounds, such as, hydroxyalkyl (meth)acrylates, glycerol mono- and di(meth)acrylate and trimethylolpropane mono- and di(meth)acrylate.

When reactive diluents A2 are mentioned in this description and in the claims, reactive diluents of the subgroup A2' are of course also included, except that the meaning is obviously limited to those reactive diluents A2 which, apart from the free-radically polymerizable olefinic double bonds, contain no further functional groups, in particular no crosslinkable functional groups.

The binders B are resins comprising free-radically polymerizable olefinic double bonds, which resins are present in the coating compositions according to the invention as particles and exhibit a melting temperature of 60 to 160°C, in particular of 80 to 160°C. The melting temperatures are not in general sharp melting points, but instead the upper end of melting ranges with a breadth of, for example, 30 to 90°C. The binders B are insoluble or virtually insoluble in the coating compositions and are present therein as particles. The binders B are only very slightly, if at all, soluble in organic solvents conventional in coatings, the solubility amounting, for example, to less than 10, in particular less than 5 g per litre of butyl acetate at 20°C.

In particular, the binders B are corresponding polyurethane resins with (meth)acryloyl groups and melting temperatures of 60 to 160°C, preferably of 80 to 160°C.

The polyurethane resins with (meth)acryloyl groups may be produced in the presence of organic solvents, which then permits the production of resins with melting temperatures at the upper end of the range of melting temperatures. It is, however, necessary to isolate the polyurethane resins obtained in this manner or remove the solvent therefrom. Preferably the production of the polyurethane resins with (meth)acryloyl groups is, however, carried out without solvent and without subsequent purification operations, although products with melting temperatures at the upper end of the melting temperature range may, at best, be produced only with difficulty. The melting temperatures of the polyurethane resins produced in the absence of organic solvent are around 60 to 140°C, in particular 80 to 140°C.

In a first preferred embodiment, the polyurethane resins with (meth)acryloyl groups are polyurethane di(meth)acrylates which can be prepared by reacting 1,6-hexane diisocyanate with a diol component and hydroxy-C2-C4-alkyl (meth)acrylate, preferably hydroxy-C2-C4-alkyl acrylate, in the molar ratio x : (x-1) : 2, wherein x means any desired value from 2 to 5, preferably, from 2 to 4, and the diol component is one single (cyclo)aliphatic diol with a molar mass of 62 to 600 or a combination of two to four, preferably of two or three of such (cyclo)aliphatic diols, wherein in the case of a diol combination each of the diols constitutes at least 10 mol % of the diols of the diol component.

The production of the polyurethane di(meth)acrylates can be carried out in the presence of organic solvent, followed by isolation of the polyurethane di(meth)acrylates so prepared. Preferably, the production of the polyurethane di(meth)acrylates is carried out without solvent and without subsequent purification operations.

1,6-hexane diisocyanate, diol component and hydroxyalkyl (meth)acrylate are reacted stoichiometrically with one another in the molar ratio x mol 1,6-hexane diisocyanate : (x-1) mol diol : 2 mol hydroxyalkyl (meth)acrylate, wherein x means any desired value from 2 to 5, preferably from 2 to 4.

One single (cyclo)aliphatic diol with a molar mass of 62 to 600 or combinations of two to four, preferably of two or three of such (cyclo)aliphatic diols are used as the diol component.

In the case of the diol combination, the diol component may be introduced as a mixture of its constituent diols or the diols constituting the diol component may be introduced individually into the synthesis. It is also possible to introduce a proportion of the diols as a mixture and to introduce the remaining proportion or proportions in the form of pure diol. Each of the diols constitutes at least 10 mol % of the diols of the diol component.

Examples of (cyclo)aliphatic diols which are possible as one single diol or as constituents of the diol component are ethylene glycol, the isomeric propane- and butanediols, 1,5-pentanediol, 1,6-hexanediol, 1,10-decanediol, 1,12-dodecanediol, neopentyl glycol, butylethylpropanediol, the isomeric cyclohexanediols, the isomeric cyclohexanedimethanols, hydrogenated bisphenol A, tricyclodecanedimethanol, and dimer fatty alcohol.

Preferred diol components are combinations, in each case amounting to 100 mol % in total, of 20 to 80 mol % hydrogenated bisphenol A with 80 to 20 mol % 1,10-decanediol, 20 to 80 mol % hydrogenated bisphenol A with 80 to 20 mol % 1,6-hexanediol, 60 to 90 mol % neopentyl glycol with 40 to 10 mol % 1,6-hexanediol, 10 to 90 mol % cyclohexanedimethanol with 90 to 10 mol % 1,5-pentanediol and three-component combinations comprising in each case 10 to 50 mol % 1,3-propanediol, 1,5-pentanediol and 1,6-hexanediol and in each case 10 to 50 mol % 1,3-propanediol, 1,5-pentanediol and cyclohexanedimethanol.

Preferably, only one hydroxy-C2-C4-alkyl (meth)acrylate is used. Examples of hydroxy-C2-C4-alkyl (meth)acrylates are hydroxyethyl (meth)acrylate, one of the isomeric hydroxypropyl (meth)acrylates or one of the isomeric hydroxybutyl (meth)acrylates; the acrylate compound is preferred in each case.

1,6-hexane diisocyanate, diol component and hydroxy-C2-C4-alkyl (meth)acrylate are preferably reacted together in the absence of solvents. The reactants may here all be reacted together simultaneously or in two or more synthesis stages. When the synthesis is performed in multiple stages, the reactants may be added in the most varied order, for example, also in succession or in alternating manner. For example, 1,6-hexane diisocyanate may be reacted initially with hydroxy-C2-C4-alkyl (meth)acrylate and then with the diol or the diols of the diol component or initially with the diol or the diols of the diol component and then with hydroxy-C2-C4-alkyl (meth)acrylate. However, the diol component may, for example, also be divided into two or more portions, for example, also into the individual diols, for example, such that 1,6-hexane diisocyanate is initially reacted with part of the diol component before further reaction with hydroxy-C2-C4-alkyl (meth)acrylate and finally, with the remaining proportion of the diol component. The individual reactants may in each case be added in their entirety or in two or more portions. The reaction is exothermic and proceeds at a temperature above the melting temperature of the reaction mixture, but below a temperature, which results in free-radical polymerization of the (meth)acrylate double bonds. The reaction temperature is, for example, 60 to a maximum of 120°C. The rate of addition or quantity of reactants added is accordingly determined on the basis of the degree of exothermy and the liquid (molten) reaction mixture may be maintained within the desired temperature range by heating or cooling.

Once the reaction carried out in the absence of solvent is complete and the reaction mixture has cooled, solid polyurethane di(meth)acrylates with calculated molar masses in the range from 630 or higher, for example, up to 2000, are obtained. The polyurethane di(meth)acrylates assume the form of a mixture exhibiting a molar mass distribution, optionally also as a mixture with the adduct, formed as a secondary product, of one molecule of 1,6-hexane diisocyanate and two molecules of hydroxy-C2-C4-alkyl (meth)acrylate. The polyurethane di(meth)acrylates do not, however, require working up and may be used directly as binder B. Their melting temperatures are in particular in the range from 80 to 120°C.

In a second preferred embodiment, the polyurethane resins with (meth)acryloyl groups are polyurethane di(meth)acrylates which can be prepared by reacting a diisocyanate component, a diol component and hydroxy-C2-C4-alkyl (meth)acrylate, preferably, hydroxy-C2-C4-alkyl acrylate, in the molar ratio x:(x-1):2, wherein x means any desired value from 2 to 5, preferably, from 2 to 4, wherein 50 to 80 mol % of the diisocyanate component is formed by 1,6-hexane diisocyanate, and 20 to 50 mol % by one or two diisocyanates, each forming at least 10 mol % of the diisocyanate component and being selected from the group consisting of toluylene diisocyanate, diphenylmethane diisocyanate, dicyclohexylmethane diisocyanate, isophorone diisocyanate, trimethylhexane diisocyanate, cyclohexane diisocyanate, cyclohexanedimethylene diisocyanate and tetramethylenexylylene diisocyanate, wherein the mol % of the respective diisocyanates add up to 100 mol %, wherein the diol component comprises no more than four different diols, and 20 to 100 mol % of the diol component is formed by at least one linear aliphatic alpha,omega-C2-C12-diol, and 0 to 80 mol % by at least one (cyclo)aliphatic diol that is different from linear aliphatic alpha,omega-C2-C12-diols, wherein each diol of the diol component forms at least 10 mol % within the diol component, and wherein the mol % of the respective diols add up to 100 mol %. Preferably, the production of the polyurethane di(meth)acrylates is carried out without solvent and without subsequent purification operations.

Diisocyanate component, diol component and hydroxy-C2-C4-alkyl (meth)acrylate are reacted stoichiometrically with one another in the molar ratio x mol diisocyanate : x-1 mol diol : 2 mol hydroxy-C2-C4-alkyl (meth)acrylate, wherein x represents any value from 2 to 5, preferably from 2 to 4.

50 to 80 mol % of the diisocyanate component is formed by 1,6-hexane diisocyanate, and 20 to 50 mol % by one or two diisocyanates selected from the group consisting of toluylene diisocyanate, diphenylmethane diisocyanate, dicyclohexylmethane diisocyanate, isophorone diisocyanate, trimethylhexane diisocyanate, cyclohexane diisocyanate, cyclohexanedimethylene diisocyanate and tetramethylenexylylene diisocyanate, wherein if two diisocyanates are selected, each diisocyanate forms at least 10 mol % of the diisocyanates of the diisocyanate component. Preferably, the diisocyanate or the two diisocyanates, forming in total 20 to 50 mol % of the diisocyanate component, are selected from dicyclohexylmethane diisocyanate, isophorone diisocyanate, trimethylhexane diisocyanate, cyclohexane diisocyanate, cyclohexanedimethylene diisocyanate and tetramethylenexylylene diisocyanate.

20 to 100 mol %, preferably, 80 to 100 mol %, of the diol component consisting of one to four, preferably, one to three, diols is formed by at least one linear aliphatic alpha, omega-C2-C12-diol, and 0 to 80 mol %, preferably, 0 to 20 mol %, by at least one (cyclo)aliphatic diol that is different from linear aliphatic alpha,omega-C2-C12-diols and preferably, also from alpha, omega-diols having more than 12 carbon atoms. Each diol of the diol component forms at least 10 mol % within the diol component.

Most preferably, the diol component does not comprise any diols that are different from linear aliphatic alpha,omega-C2-C12-diols, but rather consists of one to four, preferably, one to three, and in particular only one linear aliphatic alpha,omega-C2-C12-diol(s).

Examples of linear aliphatic alpha,omega-C2-C12-diols that may be used in the diol component include ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,10-decanediol and 1,12-dodecanediol.

Examples of (cyclo)aliphatic diols that are different from linear aliphatic alpha,omega-C2-C12-diols and may be used in the diol component include those isomers of propanediol and butanediol that are different from the isomers of propanediol and butanediol specified in the preceding paragraph, as well as, neopentyl glycol, butyl ethyl propanediol, the isomeric cyclohexanediols, the isomeric cyclohexanedimethanols, hydrogenated bisphenol A and tricyclodecanedimethanol.

If the diol component consists of more than one diol, the diols may be used as mixture in the synthesis process, or the diols forming the diol component are in each case used individually during the synthesis. It is also possible to use a portion of the diols as a mixture and the remaining fraction(s) in the form of pure diol.

Preferably, only one hydroxy-C2-C4-alkyl (meth)acrylate is used. Examples of hydroxy-C2-C4-alkyl (meth)acrylates are hydroxyethyl (meth)acrylate, one of the isomeric hydroxypropyl (meth)acrylates or one of the isomeric hydroxybutyl (meth)acrylates; the acrylate compound is preferred in each case.

The diisocyanates of the diisocyanate component, the diol or diols of the diol component and hydroxy-C2-C4-alkyl (meth)acrylate are preferably reacted with one another in substance, i.e., in the absence of a solvent. The reactants may here all be reacted together simultaneously or in two or more synthesis stages. When the synthesis is performed in multiple stages, the reactants may be added in the most varied order, for example, also in succession or in alternating manner. For example, the diisocyanates of the diisocyanate component may be reacted first with hydroxy-C2-C4-alkyl (meth)acrylate and then with the diol or diols of the diol component, or first with the diol or diols of the diol component and then with hydroxy-C2-C4-alkyl (meth)acrylate. However, the diol component may also be divided into two or more partial amounts, for example, or into the individual diols, for example, such that the diisocyanates are reacted first with a portion of the diol component, prior to the further reaction with hydroxy-C2-C4-alkyl (methyl)acrylate, and finally with the remaining proportion of the diol component, for example. Equally, however, the diisocyanate component may also be divided into two or more partial amounts, for example, or into the individual diisocyanates, for example, such that the hydroxyl components are reacted first with a portion of the diisocyanate component and finally with the remaining proportion of the diisocyanate component, for example. The individual reactants may in each case be added in their entirety or in two or more portions. The reaction is exothermic and proceeds at a temperature above the melting temperature of the reaction mixture, but below a temperature, which results in free-radical polymerization of the (meth)acrylate double bonds. The reaction temperature is, for example, 60 to a maximum of 120°C. The rate of addition or quantity of reactants added is accordingly determined on the basis of the degree of exothermy and the liquid (molten) reaction mixture may be maintained within the desired temperature range by heating or cooling.

Once the reaction carried out in the absence of solvent is complete and the reaction mixture has cooled, solid polyurethane di(meth)acrylates with calculated molar masses in the range from 628 or higher, for example, up to 2000, are obtained. The polyurethane di(meth)acrylates assume the form of a mixture exhibiting a molar mass distribution. The polyurethane di(meth)acrylates do not, however, require working up and may be used directly as binder B. Their melting temperatures are in particular in the range from 80 to 120°C.

In a third preferred embodiment, the polyurethane resins with (meth)acryloyl groups are polyurethane (meth)acrylates which can be prepared by reacting a trimer of a (cyclo)aliphatic diisocyanate, 1,6-hexanediisocyanate, a diol component and hydroxy-C2-C4 alkyl(meth)acrylate, preferably hydroxy-C2-C4 alkylacrylate, in the molar ratio 1: x : x : 3, wherein x means any desired value from 1 to 6, preferably, from 1 to 3, wherein the diol component is one single linear aliphatic alpha,omega C2-C12 diol or a combination of two to four, preferably, two or three, (cyclo)aliphatic diols, wherein in the case of diol combination, each of the diols makes up at least 10 mol % of the diols of the diol combination and the diol combination consists of at least 80 mol % of at least one linear aliphatic alpha,omega C2-C12 diol. Preferably, the production of the polyurethane (meth)acrylates is carried out without solvent and without subsequent purification operations.

The trimer of the (cyclo)aliphatic diisocyanate, 1,6-hexanediisocyanate, diol component and hydroxy-C2-C4 alkyl(meth)acrylate are reacted stoichiometrically with one another in the molar ratio 1 mol trimer of the (cyclo)aliphatic diisocyanate : x mol 1,6-hexanediisocyanate : x mol diol : 3 mol hydroxy-C2-C4 alkyl(meth)acrylate, wherein x represents any value from 1 to 6, preferably from 1 to 3.

The trimer of the (cyclo)aliphatic diisocyanate is polyisocyanates of the isocyanurate type, prepared by trimerization of a (cyclo)aliphatic diisocyanate. Appropriate trimerization products derived, for example, from 1,4-

cyclohexanedimethylenediisocyanate, in particular from isophorondiisocyanate and more particularly from 1,6-hexanediisocyanate, are suitable. The industrially obtainable isocyanurate polyisocyanates generally contain, in addition to the pure trimer, i.e., the isocyanurate made up of three diisocyanate molecules and comprising three NCO functions, isocyanate-functional secondary products with a relatively high molar mass. Products with the highest possible degree of purity are preferably used. In each case, the trimers of the (cyclo)aliphatic diisocyanates obtainable in industrial quality are regarded as pure trimer irrespective of their content of said isocyanate-functional secondary products with respect to the molar ratio of 1 mol trimer of the (cyclo)aliphatic diisocyanate : x mol 1,6-hexanediisocyanate : x mol diol : 3 mol hydroxy-C2-C4 alkyl(meth)acrylate.

One single linear aliphatic alpha,omega C2-C12 diol or combinations of two to four, preferably of two or three, (cyclo)aliphatic diols are used as the diol component. The diol combination preferably consists of two to four, in particular two or three, linear aliphatic alpha,omega C2-C12 diols.

Examples of one single linear aliphatic alpha,omega C2-C12 diol or linear aliphatic alpha,omega C2-C12 diols which can be used within the diol combination are ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,10-decanediol, 1,12-dodecanediol.

Examples of (cyclo)aliphatic diols which can be used within the diol combination in addition to the at least one linear aliphatic alpha,omega C2-C12 diol making up at least 80 mol % of the diol combination are the further isomers of propane and butane diol, different from the isomers of propane and butane diol cited in the preceding paragraph, and neopentylglycol, butylethylpropanediol, the isomeric cyclohexane diols, the isomeric cyclohexanedimethanols, hydrogenated bisphenol A and tricyclodecanedimethanol.

In the case of the diol combination, the mixture of the diols making up the combination can be used in the synthesis process or the diols making up the diol combination are each used individually in the synthesis. It is also possible to use a portion of the diols as a mixture and the remaining fraction(s) in the form of pure diol.

In the case of the diol combination, preferred diol combinations totalling 100 mol % in each case are combinations of 10 to 90 mol % 1,3-propanediol with 90 to 10 mol % 1,5-pentanediol, 10 to 90 mol % 1,3-propanediol with 90 to 10 mol % 1,6-hexanediol and 10 to 90 mol % 1,5-pentanediol with 90 to 10 mol % 1,6-hexanediol.

Preferably, only one hydroxy-C2-C4-alkyl (meth)acrylate is used. Examples of hydroxy-C2-C4-alkyl (meth)acrylates are hydroxyethyl (meth)acrylate, one of the isomeric hydroxypropyl (meth)acrylates or one of the isomeric hydroxybutyl (meth)acrylates; the acrylate compound is preferred in each case.

The trimer of the (cyclo)aliphatic diisocyanate, 1,6-hexane-diisocyanate, diol component and hydroxy-C2-C4 alkyl (meth)acrylate are preferably reacted together in the absence of solvents. The reactants may here all be reacted together simultaneously or in two or more synthesis stages. Synthesis procedures in which hydroxy-C2-C4 alkyl (meth)acrylate or diol component and the trimer of the (cyclo)aliphatic diisocyanate alone are reacted with one another are preferably avoided.

When the synthesis is performed in multiple stages, the reactants may be added in the most varied order, for example, also in succession or in alternating manner. For example, 1,6-hexanediisocyanate may be reacted initially with a mixture of the hydroxyl functional components and then with the trimer of the (cyclo)aliphatic diisocyanate or a mixture of the isocyanate functional components with the hydroxyl functional components or a mixture of the isocyanate functional components initially with hydroxy-C2-C4 alkyl(meth)acrylate and then with the diol component. In the case of a diol combination, the diol component may, for example, also be divided into two or more portions, for example, also into the individual (cyclo)aliphatic diols. The individual reactants may in each case be added in their entirety or in two or more portions. The reaction is exothermic and proceeds at a temperature above the melting temperature of the reaction mixture, but below a temperature, which results in free-radical polymerization of the (meth)acrylate double bonds. The reaction temperature is, for example, 60 to a maximum of 130°C. The rate of addition or quantity of reactants added is accordingly determined on the basis of the degree of exothermy and the liquid (molten) reaction mixture may be maintained within the desired temperature range by heating or cooling.

Once the reaction carried out in the absence of solvents is complete and the reaction mixture has cooled, solid polyurethane (meth)acrylates with number average molar masses in the range of 1,500 to 4,000 (determined by gel permeation chromatography, polystyrene gel crosslinked with divinylbenzene as the stationary phase, tetrahydrofuran as the liquid phase, polystyrene standards) are obtained. The polyurethane (meth)acrylates do not require working up and may be used directly as binder B. Their melting temperatures are in particular in the range from 80 to 130°C.

The at least one binder B is present in particulate form in the coating compositions. The average particle size of the B particles determined by means of laser diffraction is, for example, 1 to 100 µm. The B particles may be formed by grinding (milling) of the solid B resin; for example, conventional powder coat production technology may be used for that purpose. The B particles may either be stirred or mixed as a ground powder into the per se liquid coating composition or liquid constituents thereof, wherein it is possible subsequently to perform additional wet grinding or dispersing of the B particles, for example, by means of a bead mill, in the resultant suspension.

A further method for forming the B particles involves hot dissolution of binder B in a dissolution medium and subsequent particle formation during and/or after cooling, in particular, dissolving the at least one binder B in a proportion or the entirety of component A, in particular in a binder A1, with heating to the melting temperature or above, for example, to temperatures of

60 to above 160°C, whereupon the B particles may form during and/or after the subsequent cooling. The component A used as dissolution medium for the at least one binder B may here be present as such, in liquid or molten form, or as a solution in organic solvent(s). Thorough mixing or stirring is preferably performed during cooling. If the coating compositions according to the invention contain organic solvents, dissolution of the at least one binder B may also be performed with heating in organic solvent, wherein the formation of the B particles, which proceeds during and/or after the subsequent cooling, may proceed in the solvent itself or after mixing of the resultant, as yet uncooled solution with components A. By using the method of hot dissolution and subsequent particle formation during and/or after cooling, it is in particular possible to produce B particles with average particle sizes at the lower end of the range of average particle sizes, for example, in the range of 1 to 50 µm, in particular 1 to 30 µm.

As already stated, the coating compositions may contain one or more crosslinking agents C. These are then dual-cure coating compositions which, apart from curing by free-radical polymerization of olefinic double bonds of components A and B, may be cured by at least one further chemical curing mechanism involving the at least one crosslinking agent C, i.e., at least one crosslinking mechanism different from free-radical polymerization of olefinic double bonds, for example, addition and/or condensation reactions. If the coating compositions contain no crosslinking agent(s) C, they are mono-cure coating compositions.

The coating compositions may contain one or more further components D which contribute towards the resin solids content. The phrase "components D" encompasses resins without free-radically polymerizable olefinic double bonds and low molecular weight compounds with functional groups, but likewise without free-radically polymerizable olefinic double bonds. Examples are physically drying resins, which cannot be cured either by free-radical polymerization of olefinic double bonds or, as in the case of coating compositions of the dual-cure type, by other chemical means. In the case of coating compositions of the dual-cure type, components D may, for example, also be resins other than components A and B or compounds of a low molecular weight defined by the empirical formula, in each case having functional groups reactive with the at least one crosslinking agent C. Examples of functional groups are hydroxyl groups which may react with the functional groups of the crosslinking agent(s) C, i.e., in the present case of hydroxyl groups, components D are, for example, polymer polyols, such as, polyester polyols or hydroxy-functional (meth)acrylic copolymers and/or polyols such as, for example, hexanediol, trimethylolpropane, glycerol. Examples of crosslinking agents C which may be combined with components D of the polyol type are transesterification crosslinking agents; free or blocked polyisocyanate crosslinking agents; amino resin crosslinking agents, such as melamine-formaldehyde resins; and/or trisalkoxycarbonyl aminotriazine crosslinking agents.

In the case of the coating compositions according to the invention, a distinction must thus be made between mono-cure coating compositions curable by free-radical polymerization of the olefinic double bonds of components A and B, and dual-cure coating compositions which may additionally be cured by a further chemical curing mechanism and contain one or more crosslinking agents C and crosslinking partners for the crosslinking agent(s) C in the form of suitable compounds of the type A1' and/or A2' and/or D. Physically drying binders of type D may be present in both mono-cure and dual-cure type coating compositions according to the invention. In the case of coating compositions which are curable exclusively by free-radical polymerization of the olefinic double bonds of components A and B and contain neither components C nor D, the binder solids content and resin solids content are identical.

The coating compositions according to the invention may be thermally curable coating compositions (curable on supply of thermal energy, for example, heating). Preferably, however, the coating compositions are curable by UV irradiation and optionally, additionally thermally curable. While thermally curable coating compositions contain at least one thermally cleavable free-radical initiator, the coating compositions, which are curable by UV irradiation, contain at least one photoinitiator. Coating compositions that are curable by UV irradiation and are additionally thermally curable by at least one thermal crosslinking mechanism different from free-radical polymerization of olefinic double bonds, i.e., by condensation and/or addition reactions, also contain at least one photoinitiator.

Examples of thermally cleavable free-radical initiators are azo compounds, peroxide compounds and C-C-cleaving initiators.

The preferred coating compositions according to the invention curable by UV irradiation and optionally, additionally by supply of thermal energy contain one or more photoinitiators, for example, in total proportions of 0.1 to 5 wt.%, preferably of 0.5 to 3 wt.%, relative to the resin solids content. Examples of photoinitiators are benzoin and derivatives thereof, acetophenone and derivatives thereof, such as, for example, 2,2-diacetoxyacetophenone, benzophenone and derivatives thereof, thioxanthone and derivatives thereof, anthraquinone, 1-benzoylcyclohexanol, organophosphorus compounds, such as, for example, acyl phosphine oxides. The photoinitiators may be used individually or in combination.

It may be convenient for the B particles to contain the at least one photoinitiator or a proportion thereof. For example, photoinitiator may be introduced into the B particles by addition and incorporation into the molten binder B and mechanical comminution, in particular grinding, as has already been mentioned above.

In general, the coating compositions according to the invention contain organic solvent(s) and then have a solids content of, for example, 40 to 95 wt.% and an organic solvent content of, for example, 5 to 60 wt.%; the sum of the wt.-% of the solids content and the organic solvent content is here, for example, 90 to 100 wt.-% (any possible difference in the corresponding range of above 0 to 10 wt.-% to make up to the total of 100 wt.% is in general formed by volatile additives). The organic solvents are in particular conventional coating solvents, for example, glycol ethers, such as, butyl glycol, butyl diglycol, dipropylene glycol dimethyl ether, dipropylene glycol monomethyl ether, ethylene glycol dimethylether; glycol ether esters, such as, ethyl glycol acetate, butyl glycol acetate, butyl diglycol acetate, methoxypropyl acetate; esters, such as, butyl acetate, isobutyl acetate, amyl acetate; ketones, such as, methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, cyclohexanone, isophorone; alcohols, such as, methanol, ethanol, propanol, butanol; aromatic hydrocarbons, such as, xylene, Solvesso® 100 (mixture of aromatic hydrocarbons with a boiling range from 155°C to 185°C), Solvesso® 150 (mixture of aromatic hydrocarbons with a boiling range from 182°C to 202°C) and aliphatic hydrocarbons.

Apart from the initiators and optional solvents already stated, the coating compositions may contain further conventional coating additives, for example, inhibitors, levelling agents, wetting agents, anticratering agents, antioxidants and light stabilizers. The additives are used in conventional amounts known to the person skilled in the art.

The coating compositions may also contain transparent pigments, color-imparting and/or special effect-imparting pigments and/or fillers, for example, corresponding to a ratio by weight of pigment plus filler : resin solids content in the range from 0:1 to 2:1. Suitable color-imparting pigments are any conventional coating pigments of an organic or inorganic nature. Examples of inorganic or organic color-imparting pigments are titanium dioxide, iron oxide pigments, carbon black, azo pigments, phthalocyanine pigments, quinacridone pigments and pyrrolopyrrole pigments. Examples of special effect pigments are metal pigments, for example, of aluminum, copper or other metals, interference pigments, such as, for example, metal oxide-coated metal pigments, for example, iron oxide-coated aluminum, coated mica, such as, for example, titanium dioxide-coated mica, graphite effect-imparting pigments, iron oxide in flake form, liquid crystal pigments, coated aluminum oxide pigments, coated silicon dioxide pigments. Examples of fillers are silicon dioxide, aluminum silicate, barium sulfate, calcium carbonate and talc.

The coating compositions are preferably pigment-free coating compositions which may be used as clear coats or transparent sealing coats.

The coating compositions may be used for the production of single-layer coatings or for the production of one or more coating layers within a multilayer coating, such as, in particular, an automotive multilayer coating, either on an automotive body or on an automotive body part. The production of such coating layer(s) may happen in the context of automotive OEM coating or automotive refinishing. The coating compositions may in particular be used in pigment-free form for the production of an outer clear top coat layer or a transparent sealing layer of a multilayer coating. They may, for example, be used for the production of a clear top coat layer on a previously applied color-imparting and/or special effect-imparting predried base coat layer. In this case, they have the advantage of exhibiting lower solvent attack towards the base coat layer in comparison with corresponding clear coats with a comparably high solids content at a comparable application viscosity which do not contain any particulate binders B. An elevated solids content of such prior art clear coats is conventionally achieved by elevated proportions of reactive diluents of the type A2, wherein such reactive diluents exhibit unfavorable solvent-attack properties , i.e., they are capable of partially dissolving previously applied color-imparting and/or special effect-imparting, predried base coat layers.

The coating compositions may be applied by means of conventional application methods, in particular by spraying onto any desired uncoated or precoated substrates, for example, of metal or thermally stable plastics. The coating compositions according to the invention exhibit low application viscosities at a comparatively high resin solids content. This is advantageous because, in the case of spray application, it is possible to use conventional spray application units, as are used for the application of liquid coatings in industrial coating facilities.

After application, the coating layer is first of all heated briefly, for example, for 5 to 15 minutes, for example, to temperatures of 60 to 200°C. Any optionally present volatile component, in particular, organic solvents may be vaporized during such heating and the B particles are fused and may become an integral part of the resin matrix.

If the coating compositions are thermally curable coating compositions, curing may proceed during said heating and/or on further supply of thermal energy by dissociation of the free-radical initiator contained therein into free radicals and free-radical polymerization of the olefinic double bonds and, in the case of coating compositions of the dual-cure type, by an additional chemical crosslinking mechanism. The further supply of thermal energy may proceed, for example, by further heating, for example, to higher temperatures of, for example, up to 220°C.

In the case of the preferred coating compositions curable by UV irradiation, once the coating layer has been heated, it is irradiated with UV radiation for the purpose of curing. On so doing, the photoinitiator(s) dissociate(s) into free-radicals and the olefinic double bonds of components A and B undergo free-radical polymerization.

UV irradiation may, for example, proceed in a belt unit fitted with one or more UV radiation emitters or the substrates and/or the UV radiation emitter(s) are moved relative to one another during irradiation. For example, the substrates may be moved through an irradiation tunnel fitted with one or more UV radiation emitters and/or a robot equipped with one or more UV radiation emitters may guide the UV radiation emitter(s) over the substrates.

UV irradiation may proceed in one or more temporally and optionally spatially separate steps. UV irradiation may take place continuously or discontinuously (in cycles).

The preferred source of radiation comprises UV radiation sources emitting in the wave length range from 180 to 420 nm, in particular from 200 to 400 nm. Examples of such continuously operating UV radiation sources are optionally doped high, medium and low pressure mercury vapor emitters and gas discharge tubes, such as, for example, low pressure xenon lamps. Discontinuous UV radiation sources may, however, also be used. These are preferably so-called high-energy flash devices (UV flash lamps for short). The UV flash lamps may contain a plurality of flash tubes, for example, quartz tubes filled with inert gas such as xenon. The UV flash lamps have an illuminance of, for example, at least 10 megalux, preferably from 10 to 80 megalux per flash discharge. The energy per flash discharge may be, for example, 1 to 10 kJoule.

The irradiation time with UV radiation when UV flash lamps are used as the UV radiation source may be, for example, in the range from 1 millisecond to 400 seconds, preferably from 4 to 160 seconds, depending on the number of flash discharges selected. The flashes may be triggered, for example, about every 4 seconds. Curing may take place, for example, by means of 1 to 40 successive flash discharges.

If continuous UV radiation sources are used, the irradiation time may be, for example, in the range from a few seconds to about 5 minutes, preferably less than 5 minutes.

The distance between the UV radiation sources and the surface to be irradiated may be, for example, 5 to 60 cm.

If the coating layer has been applied from dual-cure type coating compositions curable by UV irradiation and additionally by supply of thermal energy, thermal energy may be supplied in conventional manner, for example, by convection and/or infrared irradiation, to cure the coating layer by means of at least one additional thermal crosslinking mechanism different from free-radical polymerization of olefinic double bonds, i.e., condensation and/or addition reactions. This additional thermal curing may be performed before, during and/or after the UV irradiation.

Examples

Examples 1a to 1l (Preparation of Polyurethane Diacrylates):

Polyurethane diacrylates were produced by reacting 1,6-hexane diisocyanate with diols and hydroxyalkyl acrylate in accordance with the following general synthesis method:

1,6-hexane diisocyanate (HDI) was initially introduced into a 2 litre four-necked flask equipped with a stirrer, thermometer and column and 0.1 wt.% methylhydroquinone and 0.01 wt.% dibutyltin dilaurate, in each case relative to the initially introduced quantity of HDI, were added. The reaction mixture was heated to 60°C. Hydroxyalkyl acrylate was then apportioned in such a manner that the temperature did not exceed 80°C. The reaction mixture was stirred at 80°C until the theoretical NCO content had been reached. Once the theoretical NCO content had been reached, the diols A, B, C were added one after the other, in each case in a manner such that a temperature of 75 to 120°C was maintained. In each case, the subsequent diol was not added until the theoretical NCO content had been reached. The reaction mixture was stirred at 120°C until no free isocyanate could be detected. The hot melt was then discharged and allowed to cool.

The melting behavior of the resultant polyurethane diacrylates was investigated by means of DSC (differential scanning calorimetry, heating rate 10 K/min).

Examples 1a to 1l are shown in Table 1. The Table states which reactants were reacted together in what molar ratios and the final temperature of the melting process measured by DSC is stated in °C.

TABLE 1

Example	Mols HDI	Mols Hydroxy-alkyl acrylate	Mols diol A	Mols diol B	Mols Diol C	Final temperature of the melting process
1a	2	2 HEA	0.8 NPG	0.2 HEX		90°C
1b	3	2 HEA	1.7 NPG	0.3 HEX		88°C
1c	3	2 HEA	1.5 NPG	0.5 HEX		99°C
1d	4	2 HEA	2.2 NPG	0.8 HEX		100°C
1e	3	2 HEA	1 HBPA	1 HEX		110°C
1f	3	2 HEA	1 HBPA	1 DEC		118°C
1g	3	2 HBA	0.7 MPD	0.7 PENT	0.6 DEC	117°C
1h	3	2 HBA	1 CHDM	1 PROP		118°C
1i	3	2 HBA	1.3 CHDM	0.7 PENT		120°C
1k	3	2 HPA	1 CHDM	0.5 PROP	0.5 PENT	118°C
1l	3	2 HPA	0.6 HEX	0.7 PENT	0.7 PROP	112°C

HDI: 1,6-hexane diisocyanate

HBA: 4-hydroxybutyl acrylate

HEA: hydroxyethyl acrylate

HPA: 2-hydroxypropyl acrylate

CHDM: 1,4-cyclohexanedimethanol

DEC: 1,10-decanediol

HBPA: hydrogenated bisphenol A

HEX: 1,6-hexanediol

MPD: 2-methyl-1,3-propanediol

NPG: neopentyl glycol

PENT: 1,5-pentanediol

PROP: 1,3-propanediol

Examples 2a to 2c (Preparation of Polyurethane Diacrylates):

Polyurethane diacrylates were produced by reacting 1,6-hexane diisocyanate, additional diisocyanate, diol component and hydroxy-C2-C4-alkyl acrylate in accordance with the following general synthesis method:

1,6-hexane diisocyanate (HDI) as well as additional diisocyanate were initially introduced into a 2 litre four-necked flask equipped with a stirrer, thermometer and column and 0.1 wt.% methylhydroquinone and 0.01 wt.% dibutyltin dilaurate, in each case relative to the initially introduced quantity of diisocyanate, were added. The reaction mixture was heated to 60°C. Hydroxyalkyl acrylate was then apportioned in such a manner that the temperature did not exceed 80°C. The reaction mixture was stirred at 80°C until the theoretical NCO content had been reached. Once the theoretical NCO content had been reached, the diols were added one after the other, in each case in a manner such that a temperature of 75 to 120°C was maintained. In each case, the subsequent diol was not added until the theoretical NCO content had been reached. The reaction mixture was stirred at 120°C until no free isocyanate could be detected. The hot melt was then discharged and allowed to cool.

The melting behavior of the resultant polyurethane diacrylates was investigated by means of DSC (heating rate 10 K/min).

Examples 2a to 2b are shown in Table 2. The Table states which reactants were reacted together and in which molar ratios and the final temperature of the melting process measured using DSC is indicated in °C.

TABLE 2

Example	Mols HDI	Mols Diisocyanate	Mols Hydroxy-alkyl acrylate	Mols Diol A	Mols Diol B	Final tempera-ture of the melting process
2a	3	2 IPDI	2 HEA	3 NPG	1 HEX	120°C
2b	3	1 IPDI	2 HEA	2 NPG	1 PROP	110°C
2c	2	1 DCMDI	2 HEA	0.8 PROP	1.2 PENT	95°C

IPDI: Isophorone diisocyanate

DCMDI: Dicyclohexylmethane diisocyanate

cf. Table 1 for other abréviations.

Examples 3a to 3k (Preparation of Polyurethane Acrylates):

Polyurethane acrylates were produced by reacting a trimer of a (cyclo)aliphatic diisocyanate, HDI, diol component and hydroxyalkyl acrylate in accordance with the following general synthesis method:

A mixture of a trimer of a diisocyanate and HDI was initially introduced into a 2 litre four-necked flask equipped with a stirrer, thermometer and column and 0.1% by weight methylhydroquinone and 0.01% by weight dibutyl tin dilaurate, in each case based on the quantity of isocyanate introduced, were added. The reaction mixture was heated to 60°C. A mixture of hydroxyalkyl acrylate and diol(s) was then added such that 110°C was not exceeded. The temperature was carefully increased to a maximum of 130°C and the mixture stirred until no more free isocyanate could be detected. The hot melt was then discharged and allowed to cool.

The melting behavior of the resultant polyurethane acrylates was investigated by means of DSC (heating rate 10 K/min).

Examples 3a to 3k are shown in Table 3. The table states which reactants were reacted together and in which molar ratios and the final temperature of the melting process measured using DSC is indicated in °C.

Table 3

Example	Mols of trimeric diisocya-nate	Mols of HDI	Mols of hydroxy-alkyl acrylate	Mols of diol A	Mols of diol B	Final temperature of the melting process
3a	1 t-HDI	3	3 HPA	3 PROP		115°C
3b	1 t-HDI	3	3 HPA	1.5 PROP	1.5 PENT	112°C
3c	1 t-HDI	3	3 HPA	2.5 PROP	0.5 PENT	111°C
3d	1 t-HDI	3	3 HEA	2.5 PROP	0.5 DEC	110°C
3e	1 t-HDI	2	3 HPA	1 PROP	1 HEX	95°C
3f	1 t-HDI	2	3 HBA	2 PENT		100°C
3g	1 t-HDI	2	3 HEA	2 HEX		120°C
3h	1 t-HDI	2.5	3 HPA	2.5 PROP		110°C
3i	1 t-HDI	3	3 HEA	3 HEX		119°C
3k	1 t-HDI	2.5	3 HEA	2.5 HEX		118°C

t-HDI; trimeric hexanediisocyanate, Desmodur® N3600 from Bayer

cf. Table 1 for further abréviations.

Example 4 (Production of a Coating Composition for Comparison Purposes):

A 40 wt.% solution of a urethane acrylate (calculated molar mass 1122, calculated functionality 3.14) in butyl acetate was produced by first dissolving 0.125 mol of NPG in butyl acetate at 65°C. 1 mol of t-HDI was then added at 65°C and the batch was heated to 70°C. Once the exothermic reaction had come to an end, the reaction was continued at 80°C until a constant NCO value was reached. 4-Methoxyphenol (inhibitor) and dibutyltin dilaurate (catalyst) were then added in a quantity of in each case 0.05 wt.%, relative to the whole batch. 2.75 mol of HBA were apportioned at 60°C in such a manner that the temperature did not exceed 80°C. Once a NCO value of < 0.1 had been reached, the solids content was then reduced with butyl acetate to a solids content of 40 wt.%.

97 parts by weight of this solution were in each case mixed with 0.1 parts by weight of a free-radically polymerizable silicone levelling additive, 1 part by weight of a light stabilizer (HALS, hindered amine light stabilizer), 0.5 parts by weight of a benzotriazole-based UV absorber, 1 part by weight of a photoinitiator from the group of alpha-hydroxyketones and 0.4 parts by weight of a photoinitiator from the group of acylphosphine oxides.

Examples 5a to 5y (Production of Coating Compositions According to the Invention):

The solid binders according to Examples 1a to 1l, 2a to 2c and 3a to 3k were in each case comminuted and ground and sieved by means of grinding and sieving methods conventional for the production of powder coatings and, in this manner, converted into binder powders with an average particle size of 50 µm (determined by means of laser diffraction).

The binder powders were mixed into the coating composition from Example 4 in each case in the ratio 100 parts by weight of coating composition : 10 parts by weight of binder powder and, in a second series of tests, in the ratio 100 parts by weight of coating composition : 30 parts by weight of binder powder. The flow times of the resultant coating compositions were determined according to DIN EN ISO 2431 with a DIN 4 cup at 20°C.

The coating composition according to Example 4 and the coating compositions according to the invention produced as described were in each case sprayed onto steel test sheets as a wedge in a dry film thickness range of 20 to 70 µm and in each case suspended for 10 minutes at an object temperature of 140°C in order to remove the solvent and cause the powder fractions to fuse and merge. The hot metal sheets were then exposed to UV radiation in order to cure the coating layers in a wedge-shaped gradient (medium pressure mercury vapor emitter with a power of 100 W/cm, object distance 14 cm, belt speed 1.5 m/min).

Cured, glossy coating layers were obtained in each case.

Comparative Example 4 and Examples 5a to 5y according to the invention are shown in Table 4. The Table shows the flow times and the measured sag limits in µm, with reference to Examples 5a to 5y in each case for an addition of 10 or 30 parts by weight of binder powder to in each case 100 parts by weight of the coating composition from comparative Example 4. The first stated value in each case here relates to the addition of 10 parts by weight of binder powder and the value stated in each case in second place to the addition of 30 parts by weight of binder powder.

Table 4

Examples	Added binder powder	Flow times (seconds)	Sag limits (µm)
4 (Comparison)	./.	22	35
5 a	1a	24/33	40/50
5 b	1b	22/35	41/53
5 c	1c	25/34	43/51
5 d	1d	22/31	38/47
5 e	1e	24/37	39/48
5 f	1f	23/35	40/51
5 g	1g	23/33	41/52
5 h	1h	23/34	39/49
5 i	1i	22/32	40/47
5 k	1k	25/33	41/48
5 l	1l	25/36	43/53
5 m	2a	22/33	38/49
5 n	2b	26/36	42/51
5 o	2c	23/31	37/45
5 p	3a	23/33	39/46
5 q	3b	22/35	41/52
5 r	3c	23/32	43/47
5 s	3d	24/37	41/43
5 t	3e	22/33	36/45
5 u	3f	23/38	43/49
5 v	3g	23/32	40/50
5 w	3h	22/32	40/49
5 x	3i	24/36	41/47
5 y	3k	22/33	37/49

Claims

What is claimed is:

1. Non-aqueous, liquid coating compositions curable by free-radical polymerization of olefinic double bonds with a resin solids content consisting of 50 to 100 wt.% of a binder solids content curable by free-radical polymerization of olefinic double bonds, 0 to 30 wt.% of at least one crosslinking agent C and 0 to 50 wt.% of at least one component D, wherein the weight percentages add up to 100 wt.%, wherein the binder solids content consists of 40 to 95 wt.% of at least one component A curable by free-radical polymerization of olefinic double bonds and 5 to 60 wt.% of at least one binder B curable by free-radical polymerization of olefinic double bonds, wherein the weight percentages of the at least one component A and the at least one binder B add up to 100 wt.%, wherein the at least one component A is liquid and/or is present in dissolved form and wherein the at least one binder B is present as particles of resin having a melting temperature of 60 to 160°C.

2. The coating compositions of claim 1, wherein the solids content is 40 to 100 wt.% and consists of the resin solids content and the optional components: pigments, fillers and non-volatile additives.

3. The coating compositions of claim 2, wherein the solids content is 40 to 95 wt.%, the organic solvent content is 5 to 60 wt.% and the sum of the wt.-% of the solids content and the organic solvent content is 90 to 100 wt.-%.

4. The coating compositions of any one of the preceding claims, wherein the at least one component A is selected from the group consisting of binders A1 and reactive diluents A2 and combinations thereof.

5. The coating compositions of any one of the preceding claims, wherein the melting temperature of the at least one binder B is the upper end of a 30 to 90°C broad melting range.

6. The coating compositions of any one of the preceding claims, wherein the solubility of the at least one binder B is less than 10 g per litre of butyl acetate at 20°C.

7. The coating compositions of any one of the preceding claims, wherein the average particle size of the B particles determined by means of laser diffraction is 1 to 100 µm.

8. The coating compositions of any one of the preceding claims, wherein the B particles are formed by grinding of solid B resin or by hot dissolution of binder B in a dissolution medium and subsequent particle formation during and/or after cooling.

9. The coating compositions of any one of the preceding claims, wherein the at least one binder B is a polyurethane resin with (meth)acryloyl groups.

10. The coating compositions of claim 9, wherein the polyurethane resin with (meth)acryloyl groups is a polyurethane di(meth)acrylate which can be prepared by reacting 1,6-hexane diisocyanate with a diol component and hydroxy-C2-C4-alkyl (meth)acrylate in the molar ratio x : (x-1) : 2, wherein x means any desired value from 2 to 5 and the diol component is one single (cyclo)aliphatic diol with a molar mass of 62 to 600 or a combination of two to four of such (cyclo)aliphatic diols wherein in the case of a diol combination each of the diols constitutes at least 10 mol % of the diols of the diol component.

11. The coating compositions of claim 9, wherein the polyurethane resin with (meth)acryloyl groups is a polyurethane di(meth)acrylate which can be prepared by reacting a diisocyanate component, a diol component and hydroxy-C2-C4-alkyl (meth)acrylate in the molar ratio x:(x-1):2, wherein x means any desired value from 2 to 5, wherein 50 to 80 mol % of the diisocyanate component is formed by 1,6-hexane diisocyanate, and 20 to 50 mol % by one or two diisocyanates, each forming at least 10 mol % of the diisocyanate component and being selected from the group consisting of toluylene diisocyanate, diphenylmethane diisocyanate, dicyclohexylmethane diisocyanate, isophorone diisocyanate, trimethylhexane diisocyanate, cyclohexane diisocyanate, cyclohexanedimethylene diisocyanate and tetramethylenexylylene diisocyanate, wherein the mol % of the respective diisocyanates add up to 100 mol %, wherein the diol component comprises no more than four different diols, and 20 to 100 mol % of the diol component is formed by at least one linear aliphatic alpha,omega-C2-C12-diol, and 0 to 80 mol % by at least one (cyclo)aliphatic diol that is different from linear aliphatic alpha,omega-C2-C12-diols, wherein each diol of the diol component forms at least 10 mol % within the diol component, and wherein the mol % of the respective diols add up to 100 mol %.

12. The coating compositions of claim 9, wherein the polyurethane resin with (meth)acryloyl groups is a polyurethane (meth)acrylate which can be prepared by reacting a trimer of a (cyclo)aliphatic diisocyanate, 1,6-hexanediisocyanate, a diol component and hydroxy-C2-C4 alkyl(meth)acrylate in the molar ratio 1: x : x : 3, wherein x means any desired value from 1 to 6, wherein the diol component is one single linear aliphatic alpha,omega C2-C12 diol or a combination of two to four (cyclo)aliphatic diols, wherein in the case of diol combination each of the diols makes up at least 10 mol % of the diols of the diol combination and the diol combination consists of at least 80 mol % of at least one linear aliphatic alpha,omega C2-C12 diol.

13. The coating compositions of any one of the preceding claims, wherein the coating compositions are selected from the group consisting of thermally curable coating compositions containing at least one thermally cleavable free-radical initiator, coating compositions curable by UV irradiation containing at least one photoinitiator and coating compositions curable by UV irradiation and additionally thermally curable by at least one crosslinking mechanism different from free-radical polymerization of olefinic double bonds and containing at least one photoinitiator.

14. A process for the preparation of a coating layer, comprising the successive steps:

1) applying a coating layer from a coating composition of any one of the preceding claims,
2) heating the coating layer so formed to vaporize optionally present volatile components and to fuse particles B and
3) curing the coating layer by 3a) supply of thermal energy in case of a thermally curable coating composition or by 3b) UV irradiation in case of a coating composition curable by UV irradiation or by 3c) UV irradiation and supply of thermal energy in case of a coating composition curable by UV irradiation and additionally thermally curable by at least one crosslinking mechanism different from free-radical polymerization of olefinic double bonds.

15. The process of claim 14, wherein the coating layer is selected from the group consisting of a single-layer coating and a coating layer within a multilayer coating.

16. The process of claim 15, wherein the coating layer within the multilayer coating is an automotive multilayer coating on a substrate selected from the group consisting of automotive bodies and body parts.

17. The process of claim 16, wherein the coating layer is selected from the group consisting of an outer clear top coat layer and a transparent sealing layer.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/67 C09D175/16

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D C08G

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

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

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 01/24946 A (E.I. DU PONT DE NEMOURS/REKOWSKI) 12 April 2001 (2001-04-12) cited in the application page 2, line 6 - page 4, line 28; claims 1-9	1
A	WO 95/35332 A (CRAY VALLEY) 28 December 1995 (1995-12-28) page 2, line 31 - page 5, line 33 page 7, line 10 - line 20; claims 1-13	1
A	WO 03/044111 A (BAYER) 30 May 2003 (2003-05-30) page 4, line 16 - line 27 page 10, line 15 - page 11, line 31; claims 1-5,7	1

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search 7 June 2006	Date of mailing of the international search report 14/06/2006
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Bourgonje, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2006/003946

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
WO 0124946	A	12-04-2001	AT	283117	T	15-12-2004
			EP	1227895	A2	07-08-2002
			ES	2226930	T3	01-04-2005
			JP	2003511224	T	25-03-2003
WO 9535332	A	28-12-1995	AT	170882	T	15-09-1998
			DE	69504696	D1	15-10-1998
			DE	69504696	T2	29-04-1999
			DK	783534	T3	07-06-1999
			EP	0783534	A1	16-07-1997
			ES	2122644	T3	16-12-1998
			GB	2290793	A	10-01-1996
			JP	10501837	T	17-02-1998
			US	6525161	B1	25-02-2003
WO 03044111	A	30-05-2003	AU	2002358484	A1	10-06-2003
			DE	10156322	A1	05-06-2003
			EP	1448735	A2	25-08-2004
			JP	2005509721	T	14-04-2005
			US	2003134125	A1	17-07-2003