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(54) **Radiation curable compositions**
- Strahlenhärtbare Zusammensetzungen
- Compositions durcissables par rayonnement

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(56) References cited:
- US-A- 4 271 258
- US-B1- 6 261 645
- US-B1- 6 359 082

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UV curable coatings are one of the fastest growing sectors in the coatings industry. In recent years, UV technology has made inroads into a number of market segments like fiber optics, optical- and pressure sensitive adhesives, automotive applications like UV cured topcoats, and UV curable powder coatings. The driving force of this development is mostly the quest for an increase in productivity of the coating and curing process. In automotive refinish applications where minor repairs need to be performed swiftly and at ambient temperature, UV technology promises to significantly increase the throughput of cars in a body shop. The development of refinish applications breaks new ground in UV technology. Safety concerns associated with the use of UV lamps in body shops as well as economic constraints will likely preclude the use of high intensity light sources. Relatively inexpensive low intensity lamps that emit only in the UV-A region of the electromagnetic spectrum are taking their place thus posing new challenges to resin developers and formulators.

UV curable coating compositions are known in the art. U.S. Patent 5,684,081 describes a radiation-curable, aqueous dispersion, although the reference is silent as to the wavelength of the radiation to be used. Also known are compositions that are curable using UV radiation having a very low UV-B content and substantially no UV-C content (see, e.g., U.S. Patent application publication 2003/0059555 and U.S. Patent 6,538,044). The compositions described in the '044 patent are fragrance protected lacquer coatings that are non-aqueous and are not based on urethane chemistry. The '555 publication describes solvent-based compositions useful as primers. The compositions therein are non-aqueous and require wiping of the coating with an organic solvent following exposure to UV radiation and before sanding of the coated part.

U.S. Patent 6,559,225 describes an aqueous polyurethane dispersion for use in lacquers and coatings. The '225 patent does not describe UV curing, and hints that the dispersions described therein can be combined with radiation-curable binders (column 5, lines 17-20). U.S. Patent 6,579,932 describes an aqueous coating composition which is a mixture of a polyurethane/acylate hybrid dispersion and a polyurethane resin with oxidative drying groups. The '932 patent does not describe UV curing.

Aqueous radiation curable dispersions are also known (see, e.g., U.S. patents 5,362,773, 6,011,078, 6,479,577, 6,521,702 and 6,541,536). Non-aqueous, radiation curable compositions are also known. WO 01/74499 describes a primer composition containing one or more compounds containing two or more ethylenically unsaturated polymerizable groups per molecule. Among the compounds described are epoxy acrylates, urethane acrylates and unsaturated polyesters. The compositions described thereafter also require significant amounts of relatively low molecular weight materials (such as ethylhexyl acrylate and isobornyl methacrylate). The ‘499 publication indicates that the compositions described therein can be cured with UV radiation using UV lamps having a UV-B:UV-A ratio of 1:1 or less and substantially no UV-C content. As in the ‘555 publication noted above, the compositions require wiping of the coating with an organic solvent following exposure to UV radiation and before sanding of the coated part. Similar compositions are described in published U.S. patent applications US 2003/0045598 and US2003/045596, and U.S. patents 4,937,173, 5,013,631, 5,213,875 and 6,509,389.

Radiation curable urethane acrylates are also described in U.S. patents 4,380,604, 6,232,360, 6,753,394 and 6,790,485. Finially, radiation curable epoxy acrylates are described in U.S. patents 5,726,255, 5,756,829, 6,359,082 and RE 37,448.

Compositions have now been discovered which can be cured with radiation having a wavelength of at least 300nm and preferably from 320nm to 450nm.

More particularly, the present invention is directed to a composition curable by radiation having a wavelength of 300nm or more, and preferably radiation having a wavelength of from about 320nm to about 450nm. The compositions of the invention do not require a solvent wipe and can be sanded immediately after exposure to the radiation. Furthermore, compositions of the invention can be used as primers, sealers, fillers, putties and top coatings on a variety of different substrates, such as metal, wood, cork, plastic, leather, textiles, felt, glass, paper, mineral or composite substrates.

The compositions of the present invention are non-aqueous compositions, which contain no ethylenically unsaturated monomer, and which comprise

A) from 1 to 99 % by weight, preferably from about 10 to about 90% by weight, and most preferably from about 25 to about 75% by weight, of an unsaturated (meth)acrylate polymer or oligomer selected from the group consisting:

a) an unsaturated urethane (meth)acrylate polymer or oligomer, which has an isocyanate group content of 1%
by weight or less and is prepared by reacting:

ai) one or more organic polyisocyanates, and
aii) an unsaturated (meth)acrylate selected from the group consisting of

1) from 0 to 100% by weight of an unsaturated polyether (meth)acrylate polyol having an OH number of from 30 to 500 (preferably from about 100 to about 400 and most preferably from about 200 to about 300), and prepared by reacting a polyether di- or polyol with acrylic and/or methacrylic acid, and
2) from 0 to 100% by weight of a mono-, di-, tri- or poly-hydroxy-C_{1}-C_{10} alkyl or C_{6}-C_{10}-aryl (meth)acrylate, wherein the percents by weight of components ai)1) and ai)2) are based on the total weight of components ai)1) and ai)2) and total 100%,

at an isocyanate to hydroxyl equivalent ratio of from 0.95:1 to 1:0.95 (and preferably 1:1),

b) an unsaturated polyether (meth)acrylate polyol having an OH number of from 30 to 100 (preferably from about 30 to about 70 and most preferably from about 35 to about 65), and prepared by reacting a polyether di- or polyol with acrylic and/or methacrylic acid, and
c) mixtures thereof,

B) from 1 to 99% by weight, preferably from about 10 to about 90% by weight, and most preferably from about 25 to about 75% by weight, of an unsaturated epoxy (meth)acrylate which is substantially free from epoxide groups and is prepared by reacting

bi) one or more organic compounds containing at least one epoxide group and having a number average molecular weight of from 130 to 1000,
bii) from 1.3 to 3.0 carboxy equivalents of organic dicarboxylic acid or anhydride having a number average molecular weight of from 98 to 166,
biii) 1 hydroxy equivalent of an hydroxyl group containing reaction product, prepared at a carboxy to hydroxyl equivalent ratio of from 0.6:1 to 0.95:1 of

1) (meth)acrylic acid and
2) tri- or tetrahydroxy ether alcohols having a number average molecular weight of from 180 to 1000 and containing at least two ethylene and/or propylene oxide units as part of an ether structure,

with the ratio of reactive equivalents of components bii) through biii) to epoxide equivalents of component bi) being at least about 1:1,

C) from 0.1 to 10% by weight, preferably from about 0.5 to about 6% by weight, and most preferably from about 1 to about 4% by weight, of one or more photoinitiators, wherein the % by weight of component C) is based on the combined weight of components A) and B) and wherein the percentages of components A) and B) total 100%, and
D) from 0 to 90% by weight of solvent or a mixture of solvents, wherein the % by weight of component D) is based on the total combined amount of components A) and B).

Component A)

Component A) is an unsaturated (meth)acrylate polymer or oligomer broadly selected from the group consisting of urethane (meth)acrylates, polyether (meth)acrylates and mixtures thereof. Useful urethane (meth)acrylates are described in U.S. patents 4,380,604 and 6,753,394. Useful epoxy acrylates are described in U.S. patents 5,726,255, and RE 37,448.

Component A)

Component A) is an unsaturated (meth)acrylate polymer or oligomer selected from the group consisting of:

a) an unsaturated urethane (meth)acrylate polymer or oligomer, which has an isocyanate group content of 1% by weight or less and is prepared by reacting:

ai) one or more organic polyisocyanates, and
[0013] As noted above, useful urethane (meth)acrylates (A1a)) are described in U.S. patents 4,380,604 and 6,753,394. Such urethane (meth)acrylates are generally prepared by reacting one more polyisocyanates with an hydroxyl group-containing unsaturated (meth)acrylate.

[0014] Suitable polyisocyanates include organic polyisocyanates having aliphatically, cycloaliphatically and/or aromatically bound isocyanate groups and generally having molecular weights of from about 144 to about 1,000, more preferably from about 168 to about 300. Suitable examples include butylene diisocyanate, hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), 3,4-(isocyanatomethyl)-methylcyclohexyl isocyanate (IMCI), trimethylhexamethylene diisocyanate (2,2,4 and/or 2,4,4-trimethyl-hexamethylene diisocyanate), the isomeric bis(4,4'-isocyanato-cyclohexyl)methanes (H12MDI), the isomeric bis(isocyanatomethyl)-methylcyclohexanes, isocyanatomethyl-1,8-octane diisocyanate, 1,4-cyclohexylene diisocyanate, 1,4-phenylene diisocyanate, 2,4- and/or 2,6-tolylene diisocyanate (TDI), 1,5-naphthylene diisocyanate, 2,4'- and/or 4,4'-diphenylmethane disiocyanate (MDI), triphenylmethane-4,4',4''-trisocyanate or their derivatives having a urethane, isocyanurate, aliphosphate, biuret, uretdione, iminooxadiazinedione structure and/or mixtures thereof as well as mixtures of aliphatic and aromatic isocyanates and/or polyisocyanates. The production of such derivatives is known and described, for example, in U.S. patents 3,124,605, 3,183,112, 3,919,218, and 4,324,879 and in European patent 798,299.

[0015] Preferably used are HDI, IPDI, TDI, H12MDI and/or isocyanurate group-containing polyisocyanates obtained by trimerization of HDI, TDI or IPDI. Particularly preferred are HDI and IPDI and mixtures thereof.

[0016] In preparing the unsaturated urethane (meth)acrylate, the polyisocyanate is reacted at an isocyanate to OH equivalent ratio of from 0.95:1 to 1:0.95 (and more preferably about 1:1) with i) an unsaturated polyester (meth)acrylate having an OH number of from about 30 to about 300, ii) a mono-, di-, tri-, or polyhydroxy C1 to C10-alkyl or C6 to C10-aryl (meth)acrylate, or iii) a mixture thereof. The resultant unsaturated urethane (meth)acrylate will have an isocyanate group content of less than 1% by weight.

[0017] Useful unsaturated polyester (meth)acrylates are prepared by reacting a polyether polyl (having an hydroxyl functionality of from 2 to 6) with acrylic and/or methacrylic acid. Suitable polyether polyls are of the type known in the polyurethane art and are generally prepared by reacting a suitable starting molecule (such as, e.g., ethylene glycol, propylene glycol, butanol, glycerol, trimethylol propane, hexane diol, pentamethyrlitol and the like) with ethylene oxide, propylene oxide or a mixture thereof. The polyether is then reacted with acrylic and/or methacrylic acid. When the unsaturated (meth)acrylate is to be used to prepare the unsaturated urethane (meth)acrylate), the polyether is selected so as to produce the (meth)acrylate having the required OH number and the components are reacted in amounts such that the resultant unsaturated polyester (meth)acrylate has an OH number of from 30 to 500, preferably from about 100 to about 400 and most preferably from about 200 to about 300. In the case where the unsaturated (meth)acrylate is to be used as an part or all of component A); the polyether is selected so as to produce the (meth)acrylate having the required OH number and the polyether and acrylic (and/or methacrylic) acid are reacted in amounts such that the resultant unsaturated polyester (meth)acrylate has an OH number of from about 30 to about 100, preferably from about 100 to about 400 and most preferably from about 200 to about 300.

[0018] Useful mono-, di-, tri-, or polyhydroxy C1 to C10-alkyl or C6 to C10-aryl (meth)acrylates are also known in the polyurethane art. Such material are prepared by reacting relatively low molecular weight diols, triols and polyls (such as ethylene glycol, propylene glycol, butanol, glycerol, trimethylol propane, hexane diol, pentamethyrlitol and the like) with acrylic and/or methacrylic acid in amounts such that the resultant product contains one or more hydroxyl groups. Specific examples include hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxypropyl acrylate, hydroxyhexyl acrylate, triglycerol diacrylate, dipentaerythritol pentaacrylate, and the corresponding methacrylates.
Component B)

[0019] Component B is an unsaturated epoxy (meth)acrylate which is substantially free from epoxide groups and is prepared by reacting

bi) one or more organic compounds containing at least one epoxide group and having a number average molecular weight of from 130 to 1000.

bii) from 1.3 to 3.0 (preferably from 1.8 to 2.2, and most preferably from 1.9 to 2.1) carboxy equivalents of organic dicarboxylic acid or anhydride having a number average molecular weight of from 98 to 166,

biii) 1 hydroxy equivalent of an hydroxyl group containing reaction product, prepared at a carboxy to hydroxyl equivalent ratio of from 0.6:1 to 0.95:1 of

1) (meth)acrylic acid and
2) tri- or tetrahydroxy ether alcohols having a number average molecular weight of from 180 to 1000 and containing at least two ethylene and/or propylene oxide units as part of an ether structure,

with the ratio of reactive equivalents of components bii) through biii) to epoxide equivalents of component bi) being at least 1:1

[0020] As noted above, useful unsaturated epoxy (meth)acrylates are described in U.S. patents 5,726,255, 6,359,082 and RE 37,448.

[0021] The epoxy (meth)acrylate used is the present invention is prepared by reacting an organic compound(s) containing epoxide groups with bii) from 1.3 to 3.0 carboxy equivalents of organic dicarboxylic acid or anhydride having a molecular weight from about 98 to about 166 and biii) 1 hydroxy equivalent of OH group-containing reaction products, which are prepared at a COOH/OH equivalent ratio of 0.6:1 to 0.95:1, of 1) (meth)acrylic acid and 2) tri- or tetrahydroxy ether alcohols having a number average molecular weight of from 180 to 1000 and containing at least two ethylene and/or propylene oxide units as part of an ether structure,

[0022] Within the context of the present invention, "compounds having epoxide groups" mean organic compounds which have a number average molecular weight (M_n) of from 130 to about 1000 and contain an average of at least one (preferably from 1.5 to 6 and more preferably from 1.5 to 2) epoxide groups per molecule. An "epoxide equivalent" means the amount of epoxide compounds in grams that contains one mole of epoxide groups.

[0023] Preferred compounds having epoxide groups are those having an epoxide equivalent weight of from 100 to 500. Examples include polyglycidylethers of polyhydric phenols such as pyrocatechol, resorcinol, hydroquinone, 4,4'-dihydroxydiphenylmethane, 2,2-bis-(4-hydroxyphenyl)-propane (bisphenol A), 4,4'dihydroxydiphenylcyclohexane, 4,4'dihydroxy-diphenylsulphone, tris-(4-hydroxyphenyl)-methane and novolaks (i.e., reaction products of mono- or polyhydric phenols with aldehydes, particularly formaldehyde, in the presence of acid catalysts). Polyglycidyl ethers of bisphenol A are preferred.

[0024] Also suitable are glycidyl ethers of monoalcohols such as n-butanol or 2-ethylhexan; glycidyl ethers of polyhydric alcohols such as butane 1,4-diol, butene 1,4-diol, hexane 1,6-diol, glycerol, trimethylolpropane, pentaerythritol and polyethylene glycols; triglycidyl isocyanurate; polyglycidyl thioethers of polyhydric thiols such as bismercaptomethylbenzene; glycidyl esters of monocarboxylic acids such as versatic acid; and glycidyl esters of polyvalent, aromatic, aliphatic and cycloaliphatic carboxylic acids such as phthalic acid diglycidyl ester, isophthalic acid diglycidyl ester, terephthalic acid diglycidyl ester, tetrahydrophthalic acid diglycidyl ester, adipic acid diglycidyl ester and hexahydrophthalic acid diglycidyl ester.

[0025] Dicarboxylic acids or dicarboxylic acid anhydrides (bii)) are selected from saturated or unsaturated aliphatic dicarboxylic acids containing 4 to 10 carbon atoms such as fumaric acid, maleic acid, succinic acid, adipic acid, sebacic acid, itaconic acid and/or the corresponding anhydrides; cycloaliphatic dicarboxylic acids or dicarboxylic acid anhydrides containing 8 to 10 carbon atoms such as tetrahydrophthalic acid, hexahydrophthalic acid, norbornene dicarboxylic acid and/or anhydrides thereof; and aromatic dicarboxylic acids containing 8 carbon atoms or anhydrides thereof such as phthalic acid, phthalic acid anhydride, isophthalic acid and terephthalic acid.

[0026] Dicarboxylic anhydrides (bii) are selected from saturated, aromatic or unsaturated (cyclo)aliphatic dicarboxylic anhydrides having 4 to 9 carbon atoms such as the anhydrides of maleic acid, succinic acid, phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid or norbornene dicarboxylic acid. In calculating the ratio of carboxy equivalents (component iii) to hydroxyl equivalent (component bii), one carboxylic anhydride group is equal to two carboxy groups.

[0027] Component biii) is selected from OH group-containing reaction products (meth)acrylic acid with tri- or tetrahydroxy ether alcohols having a number average molecular weight (determined by end group analysis) of from 180 to 1000 and containing at least two ethylene and/or propylene oxide units as part of an ether structure. These reaction products are prepared at a COOH/OH equivalent ratio of 0.6:1 to 0.95:1, preferably 0.65:1 to 0.90:1. The ether alcohols are obtained by the alkylation of suitable starter molecules in known manner. Preferred starter molecules are ether group-free tri-
or tetrahydric alcohols, which correspond to the ether alcohols. Examples include glycerol, trimethylolpropane, trimethylolpropane, pentaerythritol and mixtures thereof. The ether alcohols preferably have a degree of alkoxylation of 2 to 20, more preferably 2 to 15. The degree of alkoxylation refers to the average number of moles of ethylene oxide and/or propylene oxide which have been added onto 1 mole of an alcohol used as starter molecule.

[0028] The reaction between the components 1) and 2) takes place according to known methods, e.g., by azeotropic esterification of (meth)acrylic acid with the ether alcohols. The reaction of the epoxides with compounds bii) and biii) can also take place in one step, for example, according to the processes of DE-OS 2,429,527 and DE-A 2,534,012 (which correspond to U.S. Pat. Nos. 4,253,198 and 4,081,492, respectively), optionally in the presence of solvent. Suitable solvents include inert solvents such as butyl acetate, toluene, cyclohexane and mixtures thereof. If desired components bii) and biii) can be reacted before being reacted with the epoxide group-containing compound (see U.S. patent 5,726,255 and U.S. reissue patent 37,448). The reaction is generally carried out in the presence of about 0.01 to 3 wt. %, based on the epoxide, on catalysts such as tertiary amines, quaternary ammonium salts, alkali hydroxides, alkali salts of organic carboxylic acids, mercaptans, dialkyl sulphides, sulphonium or phosphonium compounds and phosphines. The use of quaternary ammonium salts such as triethylbenzylammonium chloride is particularly preferred. The reaction takes place at 20 to 120°C, preferably 40 to 90°C.

[0029] The epoxy(meth)acrylates may optionally be modified with basic nitrogen compounds in a amount sufficient to provide up to 0.3 NH equivalents per epoxide equivalent. The modification reaction may be carried out before or after the epoxide reaction with components bii) and biii). Suitable basic nitrogen compounds include ammonia, (cyclo)aliphatic primary or secondary mono- or polyamines, preferably having a molecular weight of 31 to 300. Examples of primary amines include mono- and diamines such as methylamine, n-butylamine, n-hexylamine, 2-ethylhexylamine, cyclohexylamine, ethanalamine, benzylamine, ethylene diamine, the isomeric dianinobutanes, the isomeric dianinohexanes and 1,4-diaminocyclohexane. Examples of secondary amines include dimethylamine, diethyamine, diethanolamine, diisopropanolamine, N-methylethanolamine and N-cyclohexylisopropylamine.

[0030] The reaction of the epoxy groups with the nitrogen compounds may optionally take place in the presence of solvents such as those previously set forth. The reaction is preferably carried out in the absence of solvent. The reaction temperature is 20 to 120°C, preferably 40 to 90°C.

[0031] The quantities of starting compounds are chosen such that the reaction leads to essentially complete conversion of the epoxy groups originally present.

[0032] In order to protect the polymerizable reaction products according to the invention from unwanted premature polymerization, it is advisable to add, during the preparation process, 0.001 to 0.2 wt. %, based on the total reaction of the epoxide groups originally present.

[0033] Component C), the photoinitiator, can be substantially any photoinitiator. A variety of photoinitiators can be utilized in the radiation-curing compositions of the present invention. The usual photoinitiators are the type that generate free radicals when exposed to radiation energy. Suitable photoinitiators include, for example, aromatic ketone compounds, such as benzophenones, allylbenzophenones, Michler's ketone, anthrone and halogenated benzophenones. Further suitable compounds include, for example, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, phenylglyoxylic acid esters, anthraquinone and the derivatives thereof, benzil ketals and hydroxyalkylphosphines. Illustrative of additional suitable photoinitiators include 2,2-dioethoxyacetophenone, 2- or 3- or 4-bromoacetophenone, 3- or 4-allyl-acetophenone, 2-acetonaphthone; benzaldehyde; benzoin; the alkyl benzoin ethers; benzophenone; benzoquinone; 1-chloroantraqui-none; p-diacetyl-benzene; 9,10-dibromoaanthracene 9,10-dichloroaanthracene; 4,4-dichlorobenzophenone; thioxanthone; isopropylthioxanthone; methylthioxanthone; α,α,α-trichloro-para-t-butyl acetophenone; 4-methoxybenzophenone; 3-chloro-8-nonylacetophenone; 3-iodo-7-methoxyxanthone; carbazole; 4-chloro-4′-benzybenzophenone; fluorene; fluorenone; 1,4-naphthylphenylketone; 1,3-pentanedione; 2,2-di-sec.-butoxy acetophenone; dimethoxyphenyl acetophe-none; propiophenone; isopropylthioxanthone; chlorothioxanthone; xanthone; maleimides and their derivatives; and mixtures thereof. There are several suitable photoinitiators commercially available from Ciba including Irgacure 184 (1-hydroxy-cyclohexyl-phenyl-ketone), Irgacure 819 (bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide), Irgacure 1850 (a 50/50 mixture of bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl-phosphate oxide and 1-hydroxy-cyclohexyl-phenyl-ketone), Irgacure 1700 (a 25/75 mixture of bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl-phosphate oxide and 2-hydroxy-2-methyl-1-phenyl-propan-1-one), Irgacure 907 (2-methyl-1-[4-(methylthio)phenyl]-2-morpholono propan-1-one), Darocur MFB (a phenyl glyoxylic acid methyl ester), Irgacure 2020 Photoinitiator blend (20% by weight of phenylbis(2,3,6-trimethylbenzoyl)phosphine oxide and 80% by weight of 2-hydroxy-2-methyl-1-phenyl-1-propanone) and Darocur 4265 (a 50/50 mixture of bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide and 2-hydroxy-2-methyl-1-phenyl-propan-
10. The formulations with or without solvents can also be loaded into aerosol containers.

Other Additives

[0037] As is known in the art and depending on the application for the coating, additional additives can be used. Such additives include dispersing agents, flow aid agents, thickening agents, defoaming agents, deaerating agents, pigments, fillers, flattening agents and wetting agents. In addition, where the article to be coated is of such a shape that portions of the coating may not be exposed to radiation, it is possible to add materials which crosslink through carboxyl, hydroxyl, amino groups or moisture. Such materials include carbodiimides, aziridines, polyvalent cations, melamine/formaldehyde, epoxies, and isocyanates. When used, such crosslinkers should be used in an amount of from 0.1 to 35% by weight based on the combined weight of components A) and B).

Applying and Curing

[0038] Generally, components A) and B) are first mixed together and then component C) and any other additives are added thereto. The composition of the invention may be applied onto the most varied substrates by spraying, rolling, knife-coating, pouring, brushing, dipping, putty knife or squeegee. Any solvent present may be then flashed off by baking in a conventional oven at a temperature of from about 20 to about 110°C preferably from about 35 to about 60°C for period of from about 1 to about 10 minutes preferably from about 4 to 8 minutes. The solvent can also be flashed off using radiation sources like infra-red or microwave.

[0039] Once the solvent has baked off, the coated substrate is subjected to UV radiation having a wavelength of at least 300nm and preferably radiation having wavelength of from about 320 to about 450nm. The distance between the surface and the radiation source will depend upon the intensity of the light source and should generally be no more than four feet. The length of time the coated substrate is subjected to the radiation will depend on the intensity and wavelength of the radiation, the distance from the radiation sources, solvent content in the formulation, temperature and the humidity of the cure surroundings but will generally be less than 15 minutes and may be as short as 0.1 second.

[0040] The cured coatings are distinguished by their sandability.

[0041] As noted above, the compositions are curable using radiation sources having wavelengths of at least 300nm and preferably from about 320 to about 450 nm. The radiation can be provided by any suitable source such as UV lamps having with or reduced infrared emission or UV lamps fitted with filters to eliminate infrared emissions or so-called LEDs (light-emitting devices) emitting radiation in the wavelength noted. Particularly useful commercially available devices include: the Panacol UV H-254 lamp (available from Panacol-Elosol GmbH) - a 250 W ozone-free, iron doped metal halide lamp with spectral wavelength of from 320 to 450nm; Panacol UVF-450 (320 nm to 450 nm depending on the black, blue or clear filter used); Honle UVA HAND 250 CUL (available from Honle UV America Inc) - emitting maximum intensity UVA range of -320 to 390 nm; PMP 250 watt metal halide lamp (available from Pro Motor Car Products Inc);
Cure-Tek UVa-400 (available from H&S Autoshot) which has a 400-watt metal halide bulb and the lamp assembly can be fitted with different filters like blue, light blue or clear to control/eliminate the infra-red radiation from the lamp source; Con-Trol-Cure Scarab-250 UV-A shop lamp system (available from UV Process Supply Inc) has a 250W iron doped metal halide lamp with a spectral wavelength output of 320 to 450 nm; Con-Trol-Cure - UV LED Cure-All 415 (available from UV Process Supply Inc. - spectral wavelength of 415 nm with a 2.5 to 7.95 W operating wattage range); Con-Trol-Cure - UV LED Cure-All 390 (available from UV Process Supply Inc. - spectral wavelength of 390 nm with a 2.76 to 9.28 W operating wattage range); UV H253 UV lamp (available from UV Light Technologies - the unit contained a 250W iron doped metal halide lamp fitted with a black glass filter to produce a spectral wavelength of between 300 and 400 nm); Radion RX10 module curing using solid state high intensity UV light source from Phoseon Technology; Low intensity microwave UV System Model QUANT-18/36 (available from Quantum Technologies - UV Intensity range: 3-30 mW/cm²; UV Spectral range: 330-390nm); WorkLED (available from Inretech Technologies using 400nm LED arrays); Flashlight MIc with 20xLEd adapter (available from Inretech Technologies using 400 nm LEDs); and Phillips TL03 lamp with radiation output above 380nm.

The examples that follow are intended to illustrate the invention without restricting its scope. Unless otherwise indicated, all percentages and parts are by weight.

The following materials were used:

**Unsaturated Acrylate Polymer A1:**

- Talc T399 - Untreated anatase pigment available from Kerr-McGee Pigments GmbH & Co.
- Barytes - Aromatic epoxy resin based on bisphenol-A and epichlorohydrin with epoxy equivalent weight of 190 available from Resolution Performance Products
- Desmodur N3600 - Low viscosity Hexamethylene Diisocyanate trimer available from Bayer MaterialScience LLC
- Epon 828 - Sparmite No.1 Barytes - Extender pigment barium sulphate from Elementis Pigments, Inc.
- CG - calcium carbonate, Vicon 15-15, available from Whittaker, Clark & Daniels, Inc.
- T399 - Talc 399, available from Whittaker, Clark & Daniels, Inc.
- B318 - an iron oxide pigment available as Bayferrox 318M from Bayer Chemical Corporation
- CD9052 - Trifunctional acid ester adhesion promoter from Sartomer Inc.
- IRG2020 - Photoinitiator Blend (20% by weight of Phenyl bis (2,4,6-trimethyl benzoyl) phosphine oxide (IB19) and 80% by weight of 2-Hydroxy-2-methyl-1-phenyl-1-propanone (D1173)) from Ciba Specialty Chemicals
- IRG819 - Irgacure 819 photoinitiator, (Phenyl bis (2,4,6-trimethyl benzoyl) phosphine oxide) available from Ciba Specialty Chemicals

**Unsaturated Acrylate Polymer A2:**

- Tronox - Untreated anatase pigment available from Kerr-McGee Pigments GmbH & Co.
- Talc - Aromatic epoxy resin based on bisphenol-A and epichlorohydrin with epoxy equivalent weight of 190 available from Resolution Performance Products
- Desmodur N3600 - Low viscosity Hexamethylene Diisocyanate trimer available from Bayer MaterialScience LLC
- Epon 828 - Sparmite No.1 Barytes - Extender pigment barium sulphate from Elementis Pigments, Inc.
- CG - calcium carbonate, Vicon 15-15, available from Whittaker, Clark & Daniels, Inc.
- T399 - Talc 399, available from Whittaker, Clark & Daniels, Inc.
- B318 - an iron oxide pigment available as Bayferrox 318M from Bayer Chemical Corporation
- CD9052 - Trifunctional acid ester adhesion promoter from Sartomer Inc.
- IRG2020 - Photoinitiator Blend (20% by weight of Phenyl bis (2,4,6-trimethyl benzoyl) phosphine oxide (IB19) and 80% by weight of 2-Hydroxy-2-methyl-1-phenyl-1-propanone (D1173)) from Ciba Specialty Chemicals
- IRG819 - Irgacure 819 photoinitiator, (Phenyl bis (2,4,6-trimethyl benzoyl) phosphine oxide) available from Ciba Specialty Chemicals

**Unsaturated Acrylate Polymer A3:**

- CD9052 - Trifunctional acid ester adhesion promoter from Sartomer Inc.
- IRG2020 - Photoinitiator Blend (20% by weight of Phenyl bis (2,4,6-trimethyl benzoyl) phosphine oxide (IB19) and 80% by weight of 2-Hydroxy-2-methyl-1-phenyl-1-propanone (D1173)) from Ciba Specialty Chemicals
- IRG819 - Irgacure 819 photoinitiator, (Phenyl bis (2,4,6-trimethyl benzoyl) phosphine oxide) available from Ciba Specialty Chemicals

**Step 1:** 86 parts of a polyether polyol with hydroxyl number 250 (trimethylol propane ethoxylated 12 times), 18.7 parts of Acrylic acid, 1.5 parts of p-toluenesulphonic acid, 0.3 parts of p-methoxyphenol and 0.02 parts of 2,5-di-tert.-butylhydroquinone were dissolved to form a 70% solution in cyclohexane, and heated to the reflux temperature while stirring and passing air through. The mixture was kept under a strong reflux until an acid number of less than 5 mg KOH/g of solids was obtained. After the mixture had cooled to 50°C, a vacuum was applied and the cyclohexane along with the water formed was distilled off. The unsaturated polyether acrylate polyol (OH number of about 70) formed is used in the next stage to form the Urethane Acrylate.

**Step 2:** 70 parts of unsaturated polyether acrylate polyol made using Step1, 10.5 parts of hydroxyl ethylacrylate, 20 parts of isophorone diisocyanate were mixed together along with and 0.01 parts of dibutyltin dilaurate and 0.01 parts of p-methoxy phenol (polymerization inhibitor). The reaction mixture was stirred at 80°C by monitoring the NCO groups using IR spectroscopy. When the isocyanate groups are completely consumed, the resultant unsaturated urethane acrylate resin had a viscosity of about 7,000 mPas measured at 23°C and a C=C content of 2.7 mol/kg.
acrylate resin had a viscosity of about 800 mPas measured at 23°C and a C=C content of 5.3 mol/kg.

Example 1:

50 parts by weight of Unsaturated Acrylate Polymer A1, 50 parts by weight of Unsaturated Epoxy Acrylate B and 7.8 parts by weight of IRG819 and were mixed together well. Then 3.4 parts by weight of TiO$_2$, 41.1 parts by weight of CC, 59 parts by weight of extender pigment T399, 0.58 parts by weight of B318M were added slowly to the resin mixture with continued stirring. The solvent-free formulation prepared was kept overnight to de-erate. The formulation was then applied to a cold rolled steel substrate to a wet film thickness of 3 mils (76.2 \( \mu \)m) using a squeegee or coatings draw-down bar or using a putty knife.

The panel was cured under a low intensity UV-A light source (Cure-Tek UVA-400 available from H&S Autoshot) for 2 minutes at a 10 inch (25.4 cm) distance resulting in a tack free surface at a dry film thickness of 1.6 to 2.0 mils (40.6-50.8 \( \mu \)m). The formulation had excellent adhesion to cold rolled steel as measured by crosshatch test (ASTM D3359-95 and General Motors GM 9071 P Tape Adhesion Tests). The coating could be sanded with #320 grit sandpaper and base coated immediately right after curing. It exhibited excellent hiding.

Example 2:

50 parts by weight of Unsaturated Acrylate Polymer A1, 50 parts by weight of Unsaturated Epoxy Acrylate B and 7.8 parts by weight of IRG819 and were mixed together well. Then 3.4 parts by weight of TiO$_2$, 41.1 parts by weight of CC, 59 parts by weight of extender pigment T399, 0.58 parts by weight of B318M, 30 parts by weight of adhesion promoter CD9052 were added slowly to the resin mixture with continued stirring. The solvent-free formulation prepared was kept overnight to de-erate. The formulation was then applied to a cold rolled steel substrate to a wet film thickness of 3 mils (76.2 \( \mu \)m) using a squeegee or coatings draw-down bar or using a putty knife.

The panel was cured under a low intensity UV-A light source (a Panacol UV H-254 lamp - 250W Ozone Free Iron doped metal halide lamp with spectral wavelength of 320-450 nm) for 2 minutes at a 1 inch (25.4 cm) distance resulting in a tack free surface at a dry film thickness of 1.6 to 2.0 mils (40.6-50.8 \( \mu \)m). The same formulation when applied to panels similarly and exposed to a low intensity UV-A light source (Cure-Tek UVA-400 available from H&S Autoshot) for 2 minutes at a 10 inch (25.4 cm) distance resulted in a tack free surface. The formulation had excellent adhesion to cold rolled steel as measured by crosshatch test (ASTM D3359-95 and General Motors GM 9071 P Tape Adhesion Tests). The coating could be sanded with #320 grit sandpaper and base coated immediately right after curing. It exhibited excellent hiding.

Example 3:

The same formulation used in Example 2 was applied in the same manner to a cold rolled steel substrate. The wet coating was then exposed to radiation from a LED source at 1/4 inch (0.64 cm) distance using a Con-Trol-Cure - UV LED Cure-All 415 device or a Con-Trol-Cure - UV LED Cure-All™ 100 array (spectral wavelength of 390nm). A tack free surface with good solvent resistance resulted. The details are shown in Table 1. The primer had excellent adhesion to cold rolled steel as measured by crosshatch test (ASTM D3359-95 and General Motors GM 9071 P Tape Adhesion Tests). The coating could be sanded with #320 grit sandpaper and base coated immediately right after curing. It exhibited excellent hiding.
Example 4:

The same formulation used in Example 2 was diluted using 60 parts of butyl acetate as solvent. The formulation was then applied to a cold rolled steel substrate by spraying with a Binks Model#2001 air-type siphon gun (air pressure 38 - 40 psi $= 0.26-0.28$ N/mm$^2$) to a wet film thickness of 4 mils (101.6 μm). The sprayed panels were air dried at room temperature for 4 minutes and then cured under a low intensity UV-A light source (a Panacol UV H-254 lamp - 250W Ozone Free Iron doped metal halide lamp with spectral wavelength of 320-450 nm) for 2 minutes at a 3 inch (7.62 cm) distance resulting in a tack free surface with a dry film thickness of 1.2 to 1.5 mils (30.5 to 38.1 μm). The sprayed panels also cured under a low intensity UV-A light source (Cure-Tek UVA-400 available from H&S Autoshot) when exposed for 2 minutes at a 10 inch (25.4 cm) distance resulting in a dry film thickness of 1.2 to 1.5 mils (30.5 to 38.1 μm). The formulations had excellent adhesion to cold rolled steel as measured by crosshatch test (ASTM D3359-95 and General Motors GM 9071 P Tape Adhesion Tests). The coating could be sanded with #320 grit sandpaper and base coated immediately right after curing. It exhibited excellent hiding.

Example 5:

50 parts by weight of Unsaturated Acrylate Polymer A1 and 50 parts by weight of Unsaturated Epoxy Acrylate B were mixed together, and 5 parts by weight of T-TIO$_2$, 25 parts by weight of extender pigment T399, 132 parts by weight of Barytes#1, 1.0 parts by weight of B318M, 10 parts by weight of adhesion promoter CD9052 were added slowly to the resin mixture with continued stirring. 4.4 parts by weight of IRG819 was dissolved in 58.45 parts by weight of butyl acetate separately and added to the dispersion mixture and stirred well. This solvent-based formulation (pigment/binder ratio = 1.5) prepared was kept overnight to de-aerate. The formulation was then applied to a cold rolled steel substrate by spraying with a Binks Model#2001 air-type siphon gun (air pressure 38 - 40 psi $= 0.26-0.28$ N/mm$^2$) to a wet film thickness of 3 mils (76.2 μm).

Example 6:

50 parts by weight of Unsaturated Acrylate Polymer A1 and 50 parts by weight of Unsaturated Epoxy Acrylate B were mixed together. 6 parts by weight of IRG819 were added slowly to the resin mixture with continued stirring. The formulation prepared was kept overnight to de-aerate. This clear formulation was then applied to a wood substrate by spraying with a Binks Model#2001 air-type siphon gun (air pressure 38 - 40 psi $= 0.26-0.28$ N/mm$^2$) to a wet film thickness of 2 mils (51 μm).
Curing the coating under a low intensity Panacol UVA 400 lamp at 10 inch distance for 8 minutes resulted in a coating with high pendulum hardness (dry film thickness of 0.9 to 1.2 mils = 22.9 to 30.5 μm). It had excellent adhesion to wood substrate as measured by crosshatch test (ASTM D3359-95 and General Motors GM 9071 P Tape Adhesion Tests). The coating could be sanded with #320 grit sandpaper and top coated immediately right after curing. It had good solvent resistance and excellent block resistance.

Example 7:

50 parts by weight of Unsaturated Acrylate Polymer A1 and 50 parts by weight of Unsaturated Epoxy Acrylate B were mixed together. 30 parts by weight of adhesion promoter CD9052 and 7.8 parts by weight of IRG819 were added slowly to the resin mixture with continued stirring. The formulation prepared was kept overnight to de-aerate. This clear formulation was then applied to a wood substrate by spraying with a Binks Model#2001 air-type siphon gun (air pressure 38 - 40 psi = 0.26-0.28 N/mm²) to a wet film thickness of 2 mils (51 μm).

Example 8:

The same formulation used in Example 7 was applied in the same manner described in Example 7 to a cold rolled steel substrate followed by exposure to radiation from an LED source at 1/4 inch (6.4 mm) distance using a Control-Cure - UV LED Cure-All™ 415 device. The details of exposure time are shown in Table 2. A tack-free surface with good solvent resistance resulted in each instance. The coating could be sanded with #320 grit sandpaper and base coated right after curing.

Example 9:

50 parts by weight of Unsaturated Acrylate Polymer A2, 50 parts by weight of Unsaturated Epoxy Acrylate B and 7.8 parts by weight of IRG819 and were mixed together well. Then 3.4 parts by weight of TiO₂, 41.1 parts by weight of CC, 59 parts by weight of extender pigment T399, 0.58 parts by weight of B318M were added slowly to the resin mixture with continued stirring. The solvent-free formulation prepared was kept overnight to de-aerate. The formulation was then applied to a cold rolled steel substrate to a wet film thickness of 6 mils (152.4 μm) using a squeegee or coatings draw-down bar or using a putty knife.

The formulation was cured under a low intensity UV-A light source (a H&S Autoshot UVA 400 lamp (with spectral wavelength of 320-450 nm) for 2 minutes at a 3 inch (7.62 cm) distance at a dry film thickness of 1.6 to 2.0 mils (40.6-50.8 μm) resulting in a tack free surface. It had excellent adhesion to cold rolled steel as measured by crosshatch test (ASTM D3359-95 and General Motors GM 9071 P Tape Adhesion Tests). The coating could be sanded with #320 grit sandpaper and base coated immediately right after curing. It exhibited excellent hiding.
Example 10:

[0066] 50 parts by weight of Unsaturated Acrylate Polymer A3, 50 parts by weight of Unsaturated Epoxy Acrylate B and 7.8 parts by weight of IRG819 and were mixed together well. Then 3.4 parts by weight of TiO₂, 41.1 parts by weight of CC, 59 parts by weight of extender pigment T399, 0.58 parts by weight of B318M were added slowly to the resin mixture with continued stirring. The solvent-free formulation prepared was kept overnight to de-aerate. The formulation was then applied to a cold rolled steel substrate to a wet film thickness of 3 mils (76.2 μm) using a squeegee or coatings draw-down bar or using a putty knife.

[0067] The formulation was cured under a low intensity UV-A light source (a H&S Autoshot UVA 400 lamp (with spectral wavelength of 320-450 nm) for 2 minutes at a 3 inch (76.2 mm) distance at a dry film thickness of 1.6 to 2.0 mils (40.6-50.8 μm) resulting in a tack free surface. It had excellent adhesion to cold rolled steel as measured by crosshatch test (ASTM D3359-95 and General Motors GM 9071 P Tape Adhesion Tests). The coating could be sanded with #320 grit sandpaper and base coated immediately right after curing. It exhibited excellent hiding.

Example 11:

[0068] 50 parts by weight of Unsaturated Acrylate Polymer A4, 50 parts by weight of Unsaturated Epoxy Acrylate B and 7.8 parts by weight of IRG819 and were mixed together well. Then 3.4 parts by weight of TiO₂, 41.1 parts by weight of CC, 59 parts by weight of extender pigment T399, 0.58 parts by weight of B318M were added slowly to the resin mixture with continued stirring. The solvent-free formulation prepared was kept overnight to de-aerate. The formulation was then applied to a cold rolled steel substrate to a wet film thickness of 3 mils (76.2 μm) using a squeegee or coatings draw-down bar or using a putty knife.

[0069] The formulation was cured under a low intensity UV-A light source (a H&S Autoshot UVA 400 lamp (with spectral wavelength of 320-450 nm) for 2 minutes at a 3 inch (76.2 mm) distance at a dry film thickness of 1.6 to 2.0 mils (40.6-50.8 μm) resulting in a tack free surface. It had excellent adhesion to cold rolled steel as measured by crosshatch test (ASTM D3359-95 and General Motors GM 9071 P Tape Adhesion Tests). The coating could be sanded with #320 grit sandpaper and base coated immediately right after curing. It exhibited excellent hiding.

Claims

1. A non-aqueous composition, which contains no ethylenically unsaturated monomer, and which comprises

   A) from 1 to 99 % by weight of an unsaturated (meth)acrylate polymer or oligomer selected from the group consisting:

   a) an unsaturated urethane (meth)acrylate polymer or oligomer, which has an isocyanate group content of 1 % by weight or less and is prepared by reacting:

   i) one or more organic polyisocyanates, and
   ii) an unsaturated (meth)acrylate selected from the group consisting of

   1) from 0 to 100% by weight of an unsaturated polyether (meth)acrylate polyl having an OH number of from 30 to 500, and prepared by reacting a polyether di- or polyol with acrylic and/or methacrylic acid, and
   2) from 0 to 100% by weight of a mono-, di-, tri- or poly-hydroxyl-C₁₀₃-C₁₀₅-alkyl or C₆-C₁₀-aryl (meth) acrylate, wherein the percents by weight of components aii) 1) and aii) 2) are based on the total weight of components aii) 1) and aii) 2 and total 100%,

   at an isocyanate to hydroxyl equivalent ratio of from 0.95:1 to 1.05,

   b) an unsaturated polyether (meth)acrylate polyl having an OH number of from 30 to 100, and prepared by reacting a polyether di- or polyol with acrylic and/or methacrylic acid, and

   c) mixtures thereof,

   B) from 1 to 99% by weight of an unsaturated epoxy (meth)acrylate which is substantially free from epoxide groups and is prepared by reacting
bi) one or more organic compounds containing at least one epoxide group and having a number average molecular weight of from 130 to 1000,
bi) from 1.3 to 3.0 carboxy equivalents of organic dicarboxylic acid or anhydride having a number average molecular weight of from 98 to 166,
biii) 1 hydroxy equivalent of an hydroxyl group containing reaction product, prepared at a carboxy to hydroxyl equivalent ratio of from 0.6:1 to 0.95:1 of
1) (meth)acrylic acid and
2) tri- or tetrahydroxy ether alcohols having a number average molecular weight of from 180 to 1000 and containing at least two ethylene and/or propylene oxide units as part of an ether structure, with the ratio of reactive equivalents of components bi) through biii) to epoxide equivalents of component bi) being at least 1:1,
C) from 0.1 to 10% by weight of one or more photoinitiators, wherein the % by weight of component C) is based on the combined weight of components A) and B) and wherein the percentages of components A) and B) total 100%, and
D) from 0 to 90% by weight of solvent or a mixture of solvents, wherein the % by weight of component D) is based on the total combined amount of components A) and B).

2. The composition of Claim 1 comprising from about 10 to about 90% by weight of component A), from about 10 to about 90% by weight of component B), and from about 0.5 to about 6% by weight of component C).

3. The composition of Claim 1 comprising from about 25 to about 75% by weight of component A), from about 25 to about 75% by weight of component B), and from about 1 to about 4% by weight of component C).

4. The composition of Claim 1, wherein component aii)1) has an OH number of from about 100 to about 400.

5. The composition of Claim 4, wherein component aii)1) has an OH number of from about 200 to about 300.

6. The composition of Claim 1 wherein the isocyanate to hydroxyl equivalent is about 1:1.

7. The composition of Claim 1, wherein the OH number of component A)(b) is from about 30 to about 70.

8. The composition of Claim 7, wherein the OH number of component A)(b) is from about 35 to about 65.

9. The composition of Claim 1, wherein from about 1.8 to about 2.2 carboxy equivalents of organic dicarboxylic acid or anhydride (component bi)) are reacted.

10. The composition of Claim 9, wherein from about 1.9 to about 2.1 carboxy equivalents of organic dicarboxylic acid or anhydride (component bi)) are reacted.

11. The composition of Claim 1, wherein component bi) contains an average of from 1.5 to 6 epoxide groups per molecule.

12. The composition of Claim 11, wherein component bi) contains an average of from 1.5 to 2 epoxide groups per molecule.

13. The composition of Claim 1, wherein the carboxy to hydroxyl equivalent ratio (component biii)) is from 0.65:1 to 0.9:1.

14. In a method of preparing a coated substrate by first applying a coating composition to said substrate and then subjecting the resultant coated substrate to radiation, the improvement wherein said composition is the composition of Claim 1 and wherein the radiation has a wavelength of 300nm or more.


Patentansprüche

1. Nichtwässrige Zusammensetzung, die kein ethylenisch ungesättigtes Monomer enthält und Folgendes umfasst:
A) 1 bis 99 Gew.-% eines ungesättigten (Meth)acrylat-Polymers oder -Oligomers, das aus der aus folgenden bestehenden Gruppe ausgewählt ist:

a) ungesättigtem Urethan-(meth)acrylat-Polymer oder -Oligomer, das einen Isocyanatgruppen-Gehalt von 1 Gew.-% oder weniger aufweist und durch Umsetzung von:

ai) einem oder mehreren organischen Polyisocyanaten und

aii) einem ungesättigten (Meth)acrylat, das aus der aus folgenden bestehenden Gruppe ausgewählt ist:

1) 0 bis 100 Gew.-% eines ungesättigten Polyether-(meth)acrylat-polyols mit einer OH-Zahl von 30 bis 500, das durch Umsetzen eines Polyetherdiols oder -polyols mit Acryl- und/oder Methacrylsäure hergestellt ist, und

2) 0 bis 100 Gew.-% eines Mono-, Di-, Tri- oder Polyhydroxy-C1-10-alkyl- oder -C8-10-aryl (meth) acrylats,

wobei die Gewichtsprozent der Komponenten ai) 1) und ai) 2) auf das Gesamtgewicht der Komponenten ai) 1) und ai) 2) bezogen sind und insgesamt 100 % ausmachen, bei einem Äquivalentverhältnis von Isocyanat zu Hydroxy von 0,95:1 bis 1:0,95 hergestellt ist,

b) einem ungesättigten Polyether-(meth)acrylatpolyol mit einer OH-Zahl von 30 bis 100, das durch Umsetzen eines Polyetherdiols oder -polyols mit Acryl- und/oder Methacrylsäure hergestellt ist, und
c) Gemischen davon,

B) 1 bis 99 Gew.-% eines ungesättigten Epoxy-(meth)acrylats, das im Wesentlichen frei von Epoxidgruppen ist und durch Umsetzung von:

bi) einer oder mehrerer organischer Verbindungen, die zumindest eine Epoxidgruppe enthalten und ein zahlenmäßiges Molekulargewicht von 130 bis 1000 aufweisen,

bii) 1,3 bis 3,0 Carboxyäquivalenten an organischer Dicarbonsäure oder deren Anhydrid mit einem zahlenmäßigen Molekulargewicht von 98 bis 166,

biii) 1 Hydroxyäquivalent eines hydroxylgruppenhaltigen Reaktionsprodukts, das bei einem Äquivalentverhältnis von Carboxy zu Hydroxy von 0,6:1 bis 0,95:1 aus

1) (Meth)acrylsäure und

2) Tri- oder Tetrahydroxyetheralkoholen mit einem zahlenmäßigen Molekulargewicht von 180 bis 1000 und zumindest zwei Ethylen- und/oder Propylenoxideinheiten als Teil einer Etherstruktur

hergestellt ist, bei einem Verhältnis der reaktiven Äquivalente der Komponenten bi) bis biii) zu den Epoxidäquivalenten von Komponente bi) von zumindest 1:1 hergestellt ist,

C) 0,1 bis 10 Gew.-% eines oder mehrerer Photoinitiatoren, worin die Gewichtsprozent der Komponente C) auf das Gewicht der Komponenten A) und B) zusammen bezogen sind und die Gewichtsprozent der Komponenten A) und B) insgesamt 100 % ausmachen, und

D) 0 bis 90 % eines Lösungsmittels oder eines Lösungsmittelgemischs, wobei die Gewichtsprozent der Komponente D) auf die kombinierte Gesamtmenge der Komponenten A) und B) bezogen sind.

2. Zusammensetzung nach Anspruch 1, die etwa 10 bis etwa 90 Gew.-% an Komponente A), etwa 10 bis etwa 90 Gew.-% an Komponente B) und etwa 0,5 bis etwa 6 Gew.-% an Komponente C) umfasst.

3. Zusammensetzung nach Anspruch 1, die etwa 25 bis etwa 75 Gew.-% an Komponente A), etwa 25 bis etwa 75 Gew.-% an Komponente B) und etwa 1 bis etwa 4 Gew.-% an Komponente C) umfasst.

4. Zusammensetzung nach Anspruch 1, worin Komponente ai) 1) eine OH-Zahl von etwa 100 bis etwa 400 aufweist.

5. Zusammensetzung nach Anspruch 4, worin Komponente ai) 1) eine OH-Zahl von etwa 200 bis etwa 300 aufweist.

6. Zusammensetzung nach Anspruch 1, worin das Äquivalentverhältnis von Isocyanat zu Hydroxy etwa 1:1 beträgt.
7. Zusammensetzung nach Anspruch 1, worin die OH-Zahl von Komponente A)b) etwa 30 bis etwa 70 beträgt.

8. Zusammensetzung nach Anspruch 7, worin die OH-Zahl von Komponente A)b) etwa 35 bis etwa 65 beträgt.

9. Zusammensetzung nach Anspruch 1, worin etwa 1,8 bis etwa 2,2 Carboxyäquivalente an organischer Dicarbonsäure oder deren Anhydrid (Komponente bii)) umgesetzt sind.

10. Zusammensetzung nach Anspruch 9, worin etwa 1,9 bis etwa 2,1 Carboxyäquivalente an organischer Dicarbonsäure oder deren Anhydrid (Komponente bii)) umgesetzt sind.

11. Zusammensetzung nach Anspruch 1, worin Komponente bi) durchschnittlich 1,5 bis 6 Epoxidgruppen pro Molekül enthält.

12. Zusammensetzung nach Anspruch 11, worin Komponente bi) durchschnittlich 1,5 bis 2 Epoxidgruppen pro Molekül enthält.

13. Zusammensetzung nach Anspruch 1, worin das Äquivalentverhältnis von Carboxy zu Hydroxy (Komponente biii)) 0,65:1 bis 0,9:1 beträgt.

14. Verfahren zur Herstellung eines beschichteten Substrats, wobei zunächst eine Beschichtungszusammensetzung auf das Substrat aufgebracht wird und das resultierende beschichtete Substrat Strahlung ausgesetzt wird, wobei die Verbesserung darin besteht, dass es sich bei der Zusammensetzung um eine Zusammensetzung nach Anspruch 1 handelt und die Strahlung eine Wellenlänge von 300 nm oder mehr aufweist.


1. Composition non aqueuse, qui ne contient aucun monomère éthyléniquement insaturé et qui comprend :

A) de 1 à 99% en poids d’un polymère ou d’oligomère de (méth)acrylate insaturé choisi parmi le groupe constitué de :

a) un polymère ou oligomère d’uréthanne (méth)acrylate insaturé, qui a une teneur en groupement isocyanate de 1% en poids ou moins et est préparé par réaction :

ai) d’un ou de plusieurs polyisocyanates organiques, et

aii) d’un (méth)acrylate insaturé choisi parmi le groupe constitué de

1) 0 à 100% en poids d’un polyéther (méth)acrylate polyol insaturé ayant un indice d’OH de 30 à 500, et préparé par réaction d’un polyéther di- ou polyol avec un acide acrylique et/ou méthacrylique, et

2) 0 à 100% en poids d’un (méth)acrylate de mono-, di-, tri- ou poly-hydroxy-alkyle en C₁-C₁₀ ou aryle en C₆-C₁₀, où les pourcentages en poids des composants aii)1) et aii)2) sont basés sur le poids total des composants aii)1) et aii)2) et le total est 100%,

à un rapport d’équivalent isocyanate à hydroxyle de 0,95:1 à 1:0,95,

b) un polyéther (méth)acrylate polyol insaturé ayant un indice d’OH de 30 à 100, et préparé par réaction d’un polyéther di- ou polyol avec un acide acrylique et/ou méthacrylique, et

c) des mélanges de ceux-ci,

B) de 1 à 99% en poids d’un époxy (méth)acrylate insaturé qui est en grande partie exempt de groupements époxyde et est préparé par réaction de

bi) un ou plusieurs composés organiques contenant au moins un groupement époxyde et ayant un poids moléculaire moyen en nombre de 130 à 1000,

bii) 1,3 à 3,0 équivalents carboxy d’acide ou d’anhydride dicarboxylique organique ayant un poids molé-
culaire moyen en nombre de 98 à 166,

biii) 1 équivalent hydroxy d’un produit de la réaction contenant un groupement hydroxyle, préparé à un rapport d’équivalent carboxy à hydroxyle de 0,6:1 à 0,95:1 de

1) un acide (méth)acrylique et
2) des tri- ou tétrahydroxy éther alcools ayant un poids moléculaire moyen en nombre de 180 à 1000 et contenant au moins deux unités d’oxyde d’éthylène et/ou de propylène comme partie d’une structure d’éther,

le rapport des équivalents réactifs des composants bii) à biii) aux équivalents époxyde du composant bi) étant au moins 1:1,

C) de 0,1 à 10% en poids d’un ou plusieurs photoinitiateurs, où le % en poids du composant C) est basé sur le poids combiné des composants A) et B) et où les pourcentages des composants A) et B) totalisent 100%, et
D) de 0 à 90% en poids de solvant ou d’un mélange de solvants, où le % en poids du composant D) est basé sur la quantité totale combinée des composants A) et B).

2. Composition selon la revendication 1 comprenant environ 10 à environ 90% en poids de composant A), environ 10 à environ 90% en poids de composant B), et environ 0,5 à environ 6% en poids de composant C).

3. Composition selon la revendication 1 comprenant environ 25 à environ 75% en poids de composant A), environ 25 à environ 75% en poids de composant B), et environ 1 à environ 4% en poids de composant C).

4. Composition selon la revendication 1, dans laquelle le composant aii) 1) a un indice d’OH environ 100 à environ 400.

5. Composition selon la revendication 4, dans laquelle le composant aii) 1) a un indice d’OH environ 200 à environ 300.

6. Composition selon la revendication 1 dans laquelle le rapport d’équivalent d’isocyanate à hydroxyle est environ 1:1.

7. Composition selon la revendication 1, dans laquelle l’indice d’OH du composant A)b) est environ 30 à environ 70.

8. Composition selon la revendication 7, dans laquelle l’indice d’OH du composant A)b) est environ 35 à environ 65.

9. Composition selon la revendication 1, dans laquelle environ 1,8 à environ 2,2 équivalents carboxy d’acide ou d’anhydride dicarboxylique organique (composant bii)) sont mis à réagir.

10. Composition selon la revendication 9, dans laquelle environ 1,9 à environ 2,1 équivalents carboxy d’acide ou d’anhydride dicarboxylique organique (composant bii)) sont mis à réagir.

11. Composition selon la revendication 1, dans laquelle le composant bi) contient une moyenne de 1,5 à 6 groupements époxyde par molécule.

12. Composition selon la revendication 11, dans laquelle le composant bi) contient une moyenne de 1,5 à 2 groupements époxyde par molécule.

13. Composition selon la revendication 1, dans laquelle le rapport d’équivalent carboxy à hydroxyle (composant biii)) est de 0,65:1 à 0,9:1.

14. Amélioration, dans un procédé de préparation d’un substrat enduit par application d’abord d’une composition de revêtement audit substrat et ensuite soumission du substrat enduit résultant au rayonnement, où ladite composition est la composition selon la revendication 1 et où le rayonnement a une longueur d’onde de 300 nm ou plus.

15. Substrat enduit préparé par le procédé selon la revendication 14.
REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 5684081 A [0002]
- US 20030059555 A [0002]
- US 6538044 B [0002]
- US 5362773 A [0004]
- US 6011078 A [0004]
- US 6479577 B [0004]
- US 6521702 B [0004]
- US 6541536 B [0004]
- US 5362773 A [0004]
- US 6011078 A [0004]
- US 6479577 B [0004]
- US 6521702 B [0004]
- US 6541536 B [0004]
- US 6232360 B [0006]
- US 6753394 B [0006] [0010] [0013]
- US 6790485 B [0006]
- US 5726555 A [0006] [0010] [0020] [0028]
- US 5756829 A [0006]
- US 6359082 B [0006] [0020]
- US RE37448 E [0006] [0020]
- DE 2429527 [0028]
- DE 2534012 A [0028]
- US 4253198 A [0028]
- US 4081492 A [0028]
- US 37448 A [0028]

Non-patent literature cited in the description