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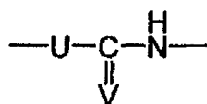
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(54) Title: RADIATION CURABLE RESIN COMPOSITION AND CURED FILM



(1)

(57) Abstract: To provide a radiation-curable resin composition exhibiting excellent curability and capable of forming a coating having high hardness, superior scratch resistance, low curling properties, superb adhesion, and excellent transparency, particularly high hardness and low curling properties, on the surface of a substrate, and a cured film of the composition. A radiation-curable resin composition comprising (A) particles produced by bonding oxide particles of at least one element selected from the group consisting of silicon, aluminum, zirconium, titanium, zinc, germanium, indium, tin, antimony, and cerium, with an organic compound including a polymerizable unsaturated group and a group shown by the following formula (1), (B) a compound containing two or more polymerizable unsaturated groups, (C) a surfactant containing a fluorine atom, and (D) an organic solvent containing one or more compounds selected from the group consisting of methanol, methyl isobutyl ketone, and n-butanol in an amount of 50 mass% or more in the total solvent. Formula (1) wherein U represents NH, O (oxygen atom), or S (sulfur atom), and V represents O or S.

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RADIATION-CURABLE RESIN COMPOSITION AND CURED FILM

The present invention relates to a radiation-curable resin composition and a cured film. More particularly, the present invention relates to a radiation-curable resin composition exhibiting excellent curability which is capable of forming a film exhibiting high hardness, excellent scratch resistance, low curling properties, excellent adhesion, and excellent transparency (high hardness and low curling properties in particular) on the surface of various substrates (e.g. plastic (polycarbonate, polymethacrylate, polymethyl methacrylate, polystyrene, polyester, polyolefin, epoxy, melamine, triacetyl cellulose, ABS resin, AS resin, norbornene resin, etc.), metal, wood, paper, glass, and slate), and to a cured film of the composition.

In recent years, a radiation-curable resin composition exhibiting excellent curability which is capable of forming coatings exhibiting high hardness, excellent scratch resistance, low curling properties, excellent adhesion, and excellent transparency has been demanded as a protective coating material for preventing scratches or stains on the surface of various substrates; an adhesive for various substrates; a sealing material; and a binder material for printing ink. Various materials containing colloidal silica have been proposed aiming at improving the scratch resistance among these required characteristics. These materials include heat-curable materials (patent documents 1 and 2) and radiation-curable materials (patent documents 3 and 4). The feature of these coating materials is that the performance of the coating materials is improved by treating the surface of silica particles with a specific organic silane or under specific conditions.

However, it is difficult to obtain a uniform film thickness in the case of applying these coating materials by using a dip coating method. Moreover, these coating materials do not necessarily satisfy all of the requirements including curability as the composition and high hardness, excellent scratch resistance, low curling properties, excellent adhesion, and excellent transparency of the resulting cured film. Since the heat-curable coating material must be subjected to heat treatment at a high temperature for a long period of time, it is difficult to apply the heat-curable coating material to a plastic substrate having low heat resistance.

Problems to be Solved by the Invention

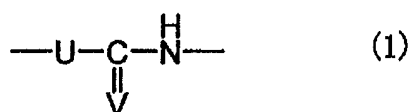
The present invention has been achieved in view of the above-described problems, and has an objective of providing a radiation-curable resin

composition exhibiting excellent curability which is capable of forming a film exhibiting high hardness, excellent scratch resistance, low curling properties, excellent adhesion, and excellent transparency (high hardness and low curling properties in particular) on the surface of various substrates, and a cured film of the composition.

5 The inventors of the present invention have conducted extensive studies in order to achieve the above objective. As a result, the inventors have found that a composition having the above-mentioned characteristics, particularly excellent hardness and low curling properties when formed into a cured film, can be obtained by a radiation-curable resin composition comprising particles obtained by bonding
10 particles of an oxide of a specific element with an organic compound having a specific group in the molecule. This finding has led to the completion of the present invention.

Specifically, the present invention provides the following radiation-curable resin composition, a cured film, and the like.

1. A radiation-curable resin composition, comprising: (A) particles produced by
15 bonding oxide particles of at least one element selected from the group consisting of silicon, aluminum, zirconium, titanium, zinc, germanium, indium, tin, antimony, and cerium, with an organic compound including a polymerizable unsaturated group and a group shown by the following formula (1); (B) a compound containing two or more polymerizable unsaturated groups; (C) a surfactant containing a fluorine atom; and (D)
20 an organic solvent containing one or more compounds selected from the group consisting of methanol, methyl isobutyl ketone, and n-butanol in an amount of 50 mass% or more in the total solvent.



25

wherein U represents NH, O (oxygen atom), or S (sulfur atom), and V represents O or S.

2. The radiation-curable resin composition according to 1, wherein the organic compound contains a group shown by [-O-C(=O)-NH-] and at least one of groups
30 shown by [-O-C(=S)-NH-] and [-S-C(=O)-NH-].

3. The radiation-curable resin composition according to 1 or 2, wherein the

organic compound is a compound containing a silanol group or a compound which produces a silanol group by hydrolysis.

4. The radiation-curable resin composition according to any of 1 to 3, wherein the surfactant (C) includes a fluorine-containing acrylic residue and a polydimethylsiloxane residue.

5. The radiation-curable resin composition according to any of 1 to 4, wherein the component (D) is a mixture of methanol, methyl isobutyl ketone, and n-butanol.

6. A cured film obtained by applying radiation to the radiation-curable resin composition according to any of 1 to 5.

7. A laminate, comprising a transparent substrate and a layer of the cured film according to 6.

According to the present invention, a radiation-curable resin composition suitable for application by a dip coating method can be obtained. In more detail, since the radiation-curable resin composition does not show uneven application and repelling, a coating in which the thickness is uniform at the center and the edge of the cured film can be obtained.

Since the radiation-curable resin composition and the cured film of the present invention have such characteristics, the radiation-curable resin composition and the cured film can be suitably used as a material for an antireflective hard coating, a hard coating for an optical sheet such as a touch panel, a hard coating for a protective plate used for a display section of a mobile instrument such as a portable telephone; and the like.

Embodiments of the radiation-curable resin composition, cured film, and laminate of the present invention are described below in detail.

I. Radiation-curable resin composition

The radiation-curable resin composition of the present invention includes (A) specific oxide particles, (B) a compound containing two or more polymerizable unsaturated groups in the molecule, (C) a surfactant containing a fluorine atom, and (D) a specific solvent as essential components, and includes (E) a polymerization initiator or the like as an optional component. The components of the composition are described below in detail.

1. Specific metal oxide particles (A)

The component (A) used in the present invention is particles prepared by bonding oxide particles of at least one element selected from the group

consisting of silicon, aluminum, zirconium, titanium, zinc, germanium, indium, tin, antimony, and cerium and a specific organic compound (hereinafter called "reactive particles").

(1) Oxide particles (Aa)

5 The oxide particles (Aa) used in the present invention are oxide particles of at least one element selected from the group consisting of silicon, aluminum, zirconium, titanium, zinc, germanium, indium, tin, antimony, and cerium from the viewpoint of colorlessness of a cured film of the resulting radiation-curable resin composition.

10 As examples of such oxides, silica, alumina, zirconia, titania, zinc oxide, germanium oxide, indium oxide, tin oxide, indium-tin oxide (ITO), antimony oxide, and cerium oxide can be given. Of these, silica, alumina, zirconia, and antimony oxide are preferable from the viewpoint of high hardness. The particles may be used either individually or in combination of two or more. The oxide particles of such
15 elements are preferably in the form of powder or a solvent dispersion sol. If the oxide particles are in the form of a solvent dispersion sol, the dispersion medium is preferably an organic solvent from the viewpoint of miscibility with other components and dispersibility of the oxide particles. As examples of the organic solvent, alcohols such as methanol, ethanol, isopropanol, butanol, and octanol; ketones such as acetone,
20 methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone; esters such as ethyl acetate, butyl acetate, ethyl lactate, and γ -butyrolactone; ethers such as ethylene glycol monomethyl ether and diethylene glycol monobutyl ether; aromatic hydrocarbons such as benzene, toluene, and xylene; and amides such as dimethylformamide, dimethylacetamide, and N-methylpyrrolidone can be given. In particular, methanol,
25 isopropanol, butanol, methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate, butyl acetate, toluene, and xylene are preferable.

 The oxide particles have a number average particle diameter of preferably 0.001 to 2 μm , still more preferably 0.001 to 0.2 μm , and particularly preferably 0.001 to 0.1 μm . If the number average particle diameter exceeds 2 μm , the
30 resulting cured film may exhibit decreased transparency, or the surface state of the resulting film may be impaired. In order to improve dispersibility of the particles, various surfactants or amines may be added.

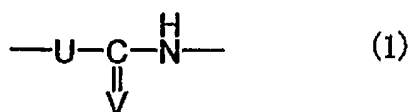
 As commercially available products of colloidal silica (silica particles), Methanol Silica Sol, IPA-ST, MEK-ST, NBA-ST, XBA-ST, DMAC-ST, ST-UP, ST-OP, ST-20, ST-40, ST-C, ST-N, ST-O, ST-50, ST-OL (manufactured by Nissan Chemical
35

Industries, Ltd.), and the like can be given. As commercially available products of powdered silica, Aerosil 130, Aerosil 300, Aerosil 380, Aerosil TT600, Aerosil OX50 (manufactured by Nippon Aerosil Co., Ltd.), Sildex H31, H32, H51, H52, H121, H122 (manufactured by Asahi Glass Co., Ltd.), E220A, E220 (manufactured by Nippon Silica Industrial Co., Ltd.), Sylsilia 470 (manufactured by Fuji Silysia Chemical, Ltd.), SG Flake (manufactured by Nippon Sheet Glass Co., Ltd.), and the like can be given.

An aqueous dispersion product of alumina is commercially available as Alumina Sol-100, Alumina Sol-200, Alumina Sol-520 (manufactured by Nissan Chemical Industries, Ltd.); an aqueous dispersion product of zinc antimonate powder is commercially available as Celnax (manufactured by Nissan Chemical Industries, Ltd.); a powder or solvent dispersion product of alumina, titanium oxide, tin oxide, indium oxide, or zinc oxide is commercially available as NanoTek (manufactured by C.I. Kasei Co., Ltd.); an aqueous dispersion sol of antimony tin oxide is commercially available as SN-100D (manufactured by Ishihara Sangyo Kaisha, Ltd.); ITO powder is commercially available from Mitsubishi Materials Corporation; and an aqueous dispersion product of cerium oxide is commercially available as Needral (manufactured by Taki Chemical Co., Ltd.). The shape of the oxide particles is globular, hollow, porous, rod, plate, fibrous, or amorphous. The oxide particles are preferably globular. The specific surface area of the oxide particles (measured by BET method using nitrogen) is preferably 10 to 1000 m²/g, and still more preferably 100 to 500 m²/g. The oxide particles may be used in the form of dry powder or a dispersion in water or an organic solvent. For example, a liquid dispersion of fine oxide particles known in the art may be used as a solvent dispersion sol of the above oxides. In particular, use of solvent dispersion sol of oxide is preferable in applications in which high transparency of the cured film is necessary.

(2) Specific organic compound (Ab)

The specific organic compound (Ab) used in the present invention is a compound containing a polymerizable unsaturated group. The organic compound (Ab) preferably further contains a group shown by the following formula (1). The organic compound (Ab) preferably contains a group [-O-C(=O)-NH-] and at least one of groups [-O-C(=S)-NH-] and [-S-C(=O)-NH-]. The specific organic compound (Ab) is preferably a compound containing a silanol group in the molecule or a compound which produces a silanol group by hydrolysis.



wherein U represents NH, O (oxygen atom), or S (sulfur atom), and V represents O or S.

5

(i) Polymerizable unsaturated group

There are no specific limitations to the polymerizable unsaturated group included in the specific organic compound (Ab). As preferable examples of the polymerizable unsaturated group, an acryloyl group, methacryloyl group, vinyl group, propenyl group, butadienyl group, styryl group, ethynyl group, cinnamoyl group, maleate group, and acrylamide group can be given.

10

The polymerizable unsaturated group is a structural unit which undergoes addition polymerization in the presence of active radical species.

15 (ii) Group shown by formula (1)

The group $[-\text{U}-\text{C}(=\text{V})-\text{NH}-]$ shown by the formula (1) included in the organic compound is $[-\text{O}-\text{C}(=\text{O})-\text{NH}-]$, $[-\text{O}-\text{C}(=\text{S})-\text{NH}-]$, $[-\text{S}-\text{C}(=\text{O})-\text{NH}-]$, $[-\text{NH}-\text{C}(=\text{O})-\text{NH}-]$, $[-\text{NH}-\text{C}(=\text{S})-\text{NH}-]$, or $[-\text{S}-\text{C}(=\text{S})-\text{NH}-]$. These groups may be used either individually or in combination of two or more. In particular, it is preferable to use the group $[-\text{O}-\text{C}(=\text{O})-\text{NH}-]$ and at least one of the groups $[-\text{O}-\text{C}(=\text{S})-\text{NH}-]$ and $[-\text{S}-\text{C}(=\text{O})-\text{NH}-]$ in combination from the viewpoint of thermal stability.

20

It is presumed that the group $[-\text{U}-\text{C}(=\text{V})-\text{NH}-]$ shown by the formula (1) causes a moderate cohesive force to occur between the molecules due to a hydrogen bond to provide the resulting cured film with properties such as excellent mechanical strength, superior adhesion to a substrate or an adjacent layer such as a high-refractive-index layer, and excellent heat resistance.

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(iii) Compound containing silanol group or compound which produces silanol group by hydrolysis

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The specific organic compound (Ab) is preferably a compound containing a silanol group in the molecule or a compound which produces a silanol

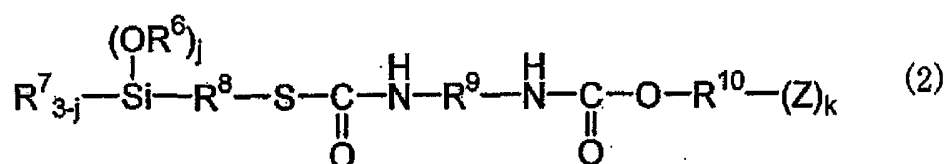
group by hydrolysis. As the compound which produces a silanol group, a compound in which an alkoxy group, aryloxy group, acetoxy group, amino group, halogen atom, or the like is bonded to a silicon atom can be given. In particular, a compound in which an alkoxy group or an aryloxy group is bonded to a silicon atom, specifically, a compound
 5 containing an alkoxysilyl group or a compound containing an aryloxysilyl group is preferable.

A silanol group or a silanol group-forming site of the compound which produces a silanol group is a structural unit which bonds to the oxide particles (Aa) by condensation or condensation occurring after hydrolysis.

10

(iv) Preferable embodiment

As a preferable example of the specific organic compound (Ab), a compound shown by the following formula (2) can be given.



15

In the formula (2), R^6 and R^7 individually represent a hydrogen atom or an alkyl group or aryl group having 1 to 8 carbon atoms, such as a methyl group, ethyl group, propyl group, butyl group, octyl group, phenyl group, or xylyl group. j
 20 represents an integer from 1 to 3.

As examples of the group shown by $[(\text{R}^6\text{O})_j\text{R}^7_{3-j}\text{Si}-]$, a trimethoxysilyl group, triethoxysilyl group, triphenoxysilyl group, methyldimethoxysilyl group, dimethylmethoxysilyl group, and the like can be given. Of these groups, a trimethoxysilyl group or a triethoxysilyl group is preferable.

25

R^8 represents a divalent organic group having an aliphatic or aromatic structure having 1 to 12 carbon atoms, and may include a linear, branched, or cyclic structure. As specific examples of such an organic group, methylene, ethylene, propylene, butylene, hexamethylene, cyclohexylene, phenylene, xylylene, dodecamethylene, and the like can be given.

30

R^9 represents a divalent organic group selected from divalent organic groups having a molecular weight of 14 to 10,000, and preferably 76 to 500. As

specific examples of such an organic group, linear polyalkylene groups such as hexamethylene, octamethylene, and dodecamethylene; divalent alicyclic or polycyclic organic groups such as cyclohexylene and norbornylene; divalent aromatic groups such as phenylene, naphthylene, biphenylene, and polyphenylene; and alkyl-

5 substituted products or aryl-substituted products of these groups can be given. These divalent organic groups may include an atomic group containing an element other than a carbon atom and a hydrogen atom, and may include a polyether bond, polyester bond, polyamide bond, or polycarbonate bond.

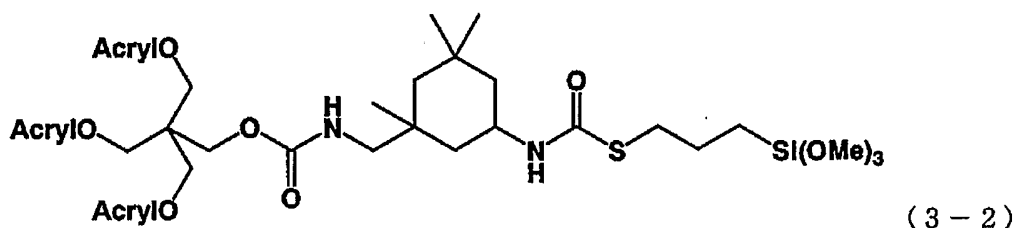
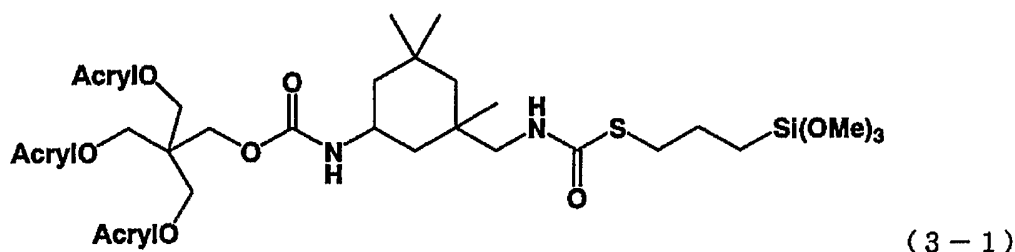
R^{10} represents an organic group with a valence of $(k+1)$, and is

10 preferably selected from linear, branched, or cyclic saturated or unsaturated hydrocarbon groups.

Z represents a monovalent organic group containing a polymerizable unsaturated group, which undergoes an intermolecular crosslinking reaction in the presence of active radical species, in the molecule. k represents an integer preferably

15 from 1 to 20, still more preferably from 1 to 10, and particularly preferably from 1 to 5.

As specific examples of the compound shown by the formula (2), compounds shown by the following formulas (3-1) and (3-2) can be given.



20

wherein "Acryl" represents an acryloyl group, and "Me" represents a methyl group.

The specific organic compound (Ab) used in the present invention may be synthesized by using a method disclosed in Japanese Patent Application Laid-open No. 9-100111, for example. The specific organic compound (Ab) is preferably

25 produced by reacting mercaptopropyltrimethoxysilane and isophorone diisocyanate at 60 to 70°C for about several hours in the presence of dibutyltin dilaurate, adding

pentaerythritol triacrylate to the reaction product, and reacting the mixture at 60 to 70°C for about several hours.

(3) Preparation of reactive particles (A)

5 The specific organic compound (Ab) containing a silanol group or a group which produces a silanol group by hydrolysis is mixed with the metal oxide particles (Aa) and hydrolyzed to bond the metal oxide particles (Aa) and the organic compound (Ab). The amount of organic polymer component (i.e. hydrolysate and condensate of hydrolysable silane) in the resulting reactive particles (A) may be
10 determined, by thermogravimetric analysis from room temperature to 800°C in air, as a constant weight loss (%) when completely burning the dry powder in air, for example.

 The amount of the specific organic compound (Ab) bonded to the oxide particles (Aa) is preferably 0.01 wt% or more, still more preferably 0.1 wt% or more, and particularly preferably 1 wt% or more of 100 wt% of the reactive particles (A)
15 (metal oxide particles (Aa) and specific organic compound (Ab) in total). If the amount of the specific organic compound (Ab) bonded to the metal oxide particles (Aa) is less than 0.01 wt%, the dispersibility of the reactive particles (A) in the composition may be insufficient, whereby the resulting cured film may exhibit insufficient transparency and scratch resistance. The amount of the metal oxide particles (Aa) in the raw material
20 when preparing the reactive particles (A) is preferably 5 to 99 wt%, and still more preferably 10 to 98 wt%. The content of the oxide particles (Aa) in the reactive particles (A) is preferably 65 to 95 wt%.

 The amount (content) of the reactive particles (A) in the curable composition is preferably 5 to 70 wt%, and still more preferably 20 to 60 wt% for 100
25 wt% of the total amount of the composition excluding the solvent. If the amount is less than 5 wt%, the resulting cured product may exhibit insufficient hardness. If the amount exceeds 70 wt%, film formability may be impaired. The amount of the reactive particles (A) refers to the solid content. When the reactive particles (A) are used in the form of a liquid dispersion, the amount of the reactive particles (A) excludes the amount
30 of dispersion medium.

2. Compound (B) containing two or more polymerizable unsaturated groups.

 The compound (B) used in the present invention is a compound containing two or more polymerizable unsaturated groups. The compound (B) is
35 suitably used to increase film-formability of the composition. There are no specific

limitations to the compound (B) insofar as the compound contains two or more polymerizable unsaturated groups. As examples of the compound (B), a (meth)acrylate and a vinyl compound can be given. Of these, a (meth)acrylate is preferable.

5 Specific examples of the compound (B) used in the present invention are given below.

 As examples of the (meth)acrylate, trimethylolpropane tri(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol
10 penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate, glycerol tri(meth)acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, ethylene glycol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, bis(2-
15 hydroxyethyl)isocyanurate di(meth)acrylate, poly(meth)acrylates of ethylene oxide or propylene oxide addition product of starting alcohols of these (meth)acrylates, oligoester (meth)acrylates, oligoether (meth)acrylates, oligourethane (meth)acrylates, and oligoepoxy (meth)acrylates having two or more (meth)acryloyl groups in the molecule, and the like can be given.

20 Of these, dipentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate, pentaerythritol tetra(meth)acrylate, and ditrimethylolpropane tetra(meth)acrylate are preferable.

 As vinyl compounds, divinylbenzene, ethylene glycol divinyl ether, diethylene glycol divinyl ether, triethylene glycol divinyl ether, and the like can be given.

25 As commercially available products of the compound (B), Aronix M-400, M-408, M-450, M-305, M-309, M-310, M-315, M-320, M-350, M-360, M-208, M-210, M-215, M-220, M-225, M-233, M-240, M-245, M-260, M-270, M-1100, M-1200, M-1210, M-1310, M-1600, M-221, M-203, TO-924, TO-1270, TO-1231, TO-595, TO-756, TO-1231, TO-1343, TO-902, TO-904, TO-905, TO-1330 (manufactured by Toagosei
30 Co., Ltd.); Kayarad D-310, D-330, DPHA, DPCA-20, DPCA-30, DPCA-60, DPCA-120, DN-0075, DN-2475, SR-295, SR-355, SR-399E, SR-494, SR-9041, SR-368, SR-415, SR-444, SR-454, SR-492, SR-499, SR-502, SR-9020, SR-9035, SR-111, SR-212, SR-213, SR-230, SR-259, SR-268, SR-272, SR-344, SR-349, SR-601, SR-602, SR-610, SR-9003, PET-30, T-1420, GPO-303, TC-120S, HDDA, NPGDA, TPGDA, PEG400DA,
35 MANDA, HX-220, HX-620, R-551, R-712, R-167, R-526, R-551, R-712, R-604, R-684,

TMPTA, THE-330, TPA-320, TPA-330, KS-HDDA, KS-TPGDA, KS-TMPTA (manufactured by Nippon Kayaku Co., Ltd.); Light Acrylate PE-4A, DPE-6A, DTMP-4A (manufactured by Kyoeisha Chemical Co., Ltd.); and the like can be given.

5 The compound (B) is used in the present invention in an amount of preferably 20 to 80 wt%, and still more preferably 40 to 75 wt% for 100 wt% of the total amount of the composition excluding the solvent. If the amount is less than 20 wt%, the resulting cured film may exhibit insufficient hardness. If the amount exceeds 80 wt%, the resulting cured film may show cure shrinkage.

10 The composition of the present invention may include a compound containing one polymerizable unsaturated group in the molecule in addition to the compound (B), as required. The type of compound containing one polymerizable unsaturated group in the molecule is not particularly limited.

3. Surfactant (C) containing fluorine atom

15 The fluorine-containing surfactant (C) is used in the present invention in order to increase applicability of the composition to a substrate. The addition of the fluorine-containing surfactant (C) also increases the hardness of the resulting cured film. As such a fluorine-containing surfactant, a nonionic or anionic fluorine-containing surfactant, or both, may be used without specific limitations. However, a nonionic
20 fluorine-containing surfactant is preferable in view of solubility in a solvent.

Specific examples include Megafac F-142D, F-144D, F-171, F-172, F-173, F-177, F-178A, F-178K, F-179, F-179A, F-183, F-184, F-191, F-812, F-815, F-1405, F410, F-443, F-445, F-450, F-471, F-472SF, F475, F-479, F-482, R-30, MCF-350, TF1025 (manufactured by Dainippon Ink and Chemicals, Inc.), EFTOP EF-101,
25 EF-121, EF-122B, EF-122C, EF-122A3, EF-121, EF-123A, EF-123B, EF-126, EF-127, EF-301, EF-302, EF-351, EF-352, EF-601, EF-801, EF-802 (manufactured by Jemco Inc.), Ftergent 250, 251, 222F, FTX-218, 212M, 245M, 290M, FTX-207S, FTX-211S, FTX-220S, FTS-230S, FTX-209F, FTX-213F, FTX-233F, FTX-245F, FTX-208G, FTX-218G, FTX-230G, FTS-240G, FTX-204D, FTX-208D, FTX-212D, FTX-216D, FTX-
30 218D, FTX-220D, FTX-222D, FTX-720C, FTX-740C (manufactured by Neos Co., Ltd.), Surfion S-111, S-112, S-113, S-121, S-131, S-132, S-141, S-145, S-381, S-383, S-393, S-101, KH-40, SA-100 (manufactured by Seimi Chemical Co., Ltd.), and the like. Of these, Megafac F-179 and F-470 and the like are preferable from the viewpoint of applicability by dip coating.

35 The fluorine-containing surfactant (C) is used in the present invention

in an amount of preferably 0.0001 to 5 wt%, and still more preferably 0.001 to 3 wt% for 100 wt% of the total amount of the composition excluding the solvent. If the amount is less than 0.0001 wt% or exceeds 5 wt%, the resulting cured film may exhibit insufficient hardness.

5

4. Solvent (D)

The composition of the present invention includes a specific solvent. Specifically, the solvent (D) includes at least one compound selected from methanol, methyl isobutyl ketone, and n-butanol in an amount of 50 wt% or more, and preferably 10 80 wt% or more of the total solvent. If the amount of the solvent (D) is less than 50 wt% of the total solvent, when applying the composition to a transparent substrate by using a dip coating method, the transparent substrate may be dissolved in the solvent depending the type of transparent substrate, so that the resulting cured film or laminate has transparency which is not suitable for optical applications. For example, in the 15 case of using only methyl ethyl ketone as the solvent, when a transparent substrate such as polycarbonate or polymethyl methacrylate is immersed in the composition by using a dip coating method, a part of the resin of the transparent substrate is dissolved in the solvent, so that the resulting cured film or laminate become cloudy. It is particularly preferable that the solvent (D) be a mixture of methanol, methyl isobutyl 20 ketone, and n-butanol.

5. Polymerization initiator (E)

The composition of the present invention may include (E) a polymerization initiator in addition to the components (A), (B), (C), and (D), as required. 25 A method of curing the composition of the present invention is described below in relation to use of the polymerization initiator (E).

The composition of the present invention is cured by application of heat and/or radiation.

In the case of curing the composition by application of heat, an 30 electric heater, infrared ray lamp, hot blast, or the like may be used as a heat source.

When radioactive rays are used, there are no specific limitations to the source of the radioactive rays so long as the composition can be cured in a short period of time after coating. As the source of infrared rays, for example, a lamp, resistance heating plate, laser, and the like can be given. As examples of the source of 35 visible rays, sunlight, a lamp, fluorescent lamp, laser, and the like can be given. As the

source of ultraviolet rays, a mercury lamp, halide lamp, laser, and the like can be given. As examples of the source of electron beams, a system of utilizing thermoelectrons produced by a commercially available tungsten filament, a cold cathode method generating electron beams by passing a high voltage pulse through a metal, and a
5 secondary electron method which utilizes secondary electrons produced by collision of ionized gaseous molecules and a metal electrode can be given. As the source of α -rays, β -rays, and γ -rays, fissionable materials such as ^{60}Co and the like can be given. As the source of γ -rays, a vacuum tube which causes accelerated electrons to collide against anodes and the like can be used. The radiation may be used either individually
10 or in combination of two or more types. One or more types of radiation may be irradiated at specific intervals of time. A polymerization initiator (E) may be added to shorten the period of time to cure the composition of the present invention. Compounds commonly used as a polymerization initiator which can produce active radicals by heat or by irradiation of radioactive rays can be used as the polymerization
15 initiator (E).

In the present invention, it is desirable to use a radiation-active initiator as the polymerization initiator (E). Particularly, the use of a radiation-active initiator (e) including either or both of an aryl ketone having a 1-hydroxycyclohexyl group and an aryl ketone having an N-morpholino group (hereinafter may be called
20 radiation-active initiator (e)) is desirable. If only the arylketone having a 1-hydroxycyclohexyl group is added, a cured film with a small degree of coloration can be formed in a short period of time. If only the arylketone having an N-morpholino group is added, a cured film with high surface hardness can be formed in a short period of time. Combined use of these compounds enables a cured film with a small degree of
25 coloration and high surface hardness to be formed in a short period of time.

There are no specific limitations to the arylketone having a 1-hydroxycyclohexyl group. As examples of the arylketone having a 1-hydroxycyclohexyl group, 1-hydroxycyclohexyl phenyl ketone, 1-hydroxycyclohexyl isopropylphenyl ketone, 1-hydroxycyclohexyldodecyl phenyl ketone, and the like can be given. There
30 are no specific limitations to the arylketone having an N-morpholino group used in the present invention. As examples of the arylketone having an N-morpholino group, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1, 2-methyl-1-[4-(methoxy)phenyl]-2-morpholinopropanone-1, 2-methyl-1-[4-(2-hydroxyethoxy)phenyl]-2-morpholinopropanone-1, 2-methyl-1-[4-(dimethylamino)phenyl]-2-
35 morpholinopropanone-1, 2-methyl-1-[4-(diphenylamino)phenyl]-2-

morpholinopropanone-1, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1, 3,6-bis(2-methyl-2-morpholinopropionyl)-9-N-octylcarbazole, and the like can be given. These radiation-active polymerization initiators (e) can be used either individually or in combinations of two or more types. To increase the cure speed and the hardness of the cured film both the surface area and inside the products, a combined use of the aryl ketones having 1-hydroxycyclohexyl group and the aryl ketones having an N-morpholino group is preferable.

As commercially available products of such a radiation-active initiator (e), Irgacure 184, 907, and the like manufactured by Ciba Specialty Chemicals Co., Ltd., for example, can be given.

The polymerization initiator (E), which is used in the present invention as an optional component, is used in an amount of preferably 0.01 to 20 wt%, and still more preferably 0.1 to 10 wt% for 100 wt% of the total amount of the composition excluding the solvent. If the amount is less than 0.01 wt%, the resulting cured film may exhibit insufficient hardness. If the amount exceeds 20 wt%, the inside (lower layer) of the resulting cured film may remain uncured.

When using the arylketone having a 1-hydroxycyclohexyl group and the arylketone having an N-morpholino group in combination, the ratio by weight of the arylketone having a 1-hydroxycyclohexyl group to the arylketone having an N-morpholino group is preferably from 10:90 to 90:10, and still more preferably from 40:60 to 80:20.

6. Other components (F)

Various components such as photosensitizers, oxide particles other than the reactive particles (A), and antioxidants may be added to the composition of the present invention, as required. Specific examples are given below.

(1) Sensitizer

As examples of sensitizers, triethylamine, diethylamine, N-methyldiethanoleamine, ethanolamine, 4-dimethylaminobenzoic acid, methyl 4-dimethylaminobenzoate, ethyl 4-dimethylaminobenzoate, isoamyl 4-dimethylaminobenzoate, and the like can be given. As commercially available products of sensitizers, Kayacure DMBI, EPA (manufactured by Nippon Kayaku Co., Ltd.), and the like can be given.

(2) Oxide particles other than reactive particles (A)

Oxide particles which are not bonded with an organic compound, for example, can be given as oxide particles other than the reactive particles (A).

(3) Additives

5 As additives, for example, antioxidants, UV absorbers, light stabilizers, silane coupling agents, aging preventives, thermal polymerization inhibitors, coloring agents, leveling agents, surfactants, preservatives, plasticizers, lubricants, inorganic fillers, organic fillers, fillers, wettability improvers, coating surface improvers, and the like can be given.

10 As commercially available products of antioxidants, Irganox 1010, 1035, 1076, 1222 (manufactured by Ciba Specialty Chemicals Co., Ltd.), and the like can be given; as commercially available products UV absorbers Tinuvin P, 234, 320, 326, 327, 328, 213, 400 (manufactured by Ciba Specialty Chemicals Co., Ltd.), Sumisorb 110, 130, 140, 220, 250, 300, 320, 340, 350, 400 (manufactured by
15 Sumitomo Chemical Industries Co., Ltd.), and the like can be given; as commercially available products of light stabilizers, Tinuvin 292, 144, 622LD (manufactured by Ciba Specialty Chemicals Co., Ltd.), Sanol LS-770, 765, 292, 2626, 1114, 744 (manufactured by Sankyo Chemical Co.), and the like can be given; as silane coupling
20 agents, γ -aminopropyltriethoxysilane, γ -mercaptopropyltrimethoxysilane, γ -methacryloxypropyltrimethoxysilane, and the like can be given; as commercially available products of these silane coupling agents, SH6062, SZ6030 (manufactured by Toray-Dow Corning Silicone Co., Ltd.), KBE903, KBM803 (manufactured by a Shin-Etsu Silicone Co., Ltd.), and the like can be given; and as commercially available
25 products of aging preventives, Antigen W, S, P, 3C, 6C, RD-G, FR, AW (manufactured by Sumitomo Chemical Industries Co., Ltd.), and the like can be given.

The composition of the present invention is suitable as a coating material. Plastic (e.g. polycarbonate, polymethacrylate, polymethyl methacrylate, polystyrene, polyester, polyolefin, epoxy, melamine, triacetyl cellulose, ABS, acrylonitrile-styrene resin, and norbornene resin), metal, wood, paper, glass, slate, and
30 the like can be given as examples of the substrate to which the composition is applied. The substrate may be in the shape of a plate, a film, or a three-dimensional formed product. As the coating method, an ordinary coating method such as dipping, spray coating, flow coating, shower coating, roll coating, spin coating, or brush coating can be given. The thickness of the coating formed by using such a coating method is usually
35 0.1 to 400 μm , and preferably 1 to 200 μm after drying and curing.

II. Cured film

The cured film of the present invention may be obtained by applying the radiation-curable resin composition to a substrate, such as a plastic substrate, and curing the composition. Specifically, the cured product is obtained as a coated formed product by applying the composition to the substrate, drying volatile components at a temperature preferably from 0 to 200°C, and curing the composition by application of heat and/or radiation. When curing the composition by applying heat, the composition is preferably cured at 20 to 150°C for 10 seconds to 24 hours. In the present invention, radiation refers to infrared rays, visible rays, ultraviolet rays, deep ultraviolet rays, X-rays, electron beams, α -rays, β -rays, γ -rays, and the like. When curing the composition by applying radiation, it is preferable to use ultraviolet rays or electron beams. Ultraviolet rays are irradiated at a dose preferably from 0.01-10 J/cm², and more preferably from 0.1 to 2 J/cm². Electron beams are preferably applied at an accelerating voltage of 10 to 300 KV, an electron density of 0.02 to 0.30 mA/cm², and a dose of 1 to 10 Mrad.

Because the cured film of the present invention exhibits high hardness, superior scratch resistance, low curling properties, excellent adhesion and transparency, particularly outstanding high hardness and low curling properties, the film can be used as a protective coating material to prevent stains or scratches on plastic optical parts, touch panels, film-type liquid crystal elements, plastic containers, or flooring materials, wall materials, and artificial marbles which are used for architectural interior finishes, (particularly as a hard coating material for plastic sheets and plastic films requiring transparency); as an adhesive for various substrates, a sealing material, and a vehicle for printing ink; and the like. Other application areas include cathode-ray tubes, front panels and device parts of flat displays (laser displays, photochromic displays, electrochromic displays, liquid crystal displays, plasma displays, light-emitting diode displays, electroluminescent panels, etc.), front covers for enclosure cases, optical lenses, spectacles, windshields, light enclosure, helmet shield, and the like.

III. Laminate

The cured film of the present invention is usually laminated on a substrate as a hard coating layer. A laminate suitable as an antireflective film may be formed by laminating a high-refractive-index layer and a low-refractive-index layer on the cured film (hard coating layer). The antireflective film may further include another

layer. For example, pairs of a high-refractive-index layer and a low-refractive-index layer may be provided to form a wide-band antireflective film having relatively uniform reflectance characteristics for light over a wide wavelength range. Or, an antistatic layer may be provided.

5 There are no specific limitations to the substrate. When using the laminate as an antireflective film, plastic (e.g. polycarbonate, polymethyl methacrylate, polystyrene, polyester, polyolefin, epoxy resin, melamine resin, triacetyl cellulose resin, ABS resin, AS resin, and norbornene resin) and the like can be given as the material for the substrate.

10 As the high-refractive-index film used for the laminate of the invention, a coating material cured film having a refractive index of 1.65 to 2.20 and containing metal oxide particles such as zirconia particles can be given, for example.

 As examples of the low-refractive-index film used in the present invention, a film having a refractive index of 1.38 to 1.45, such as a metal oxide film or
15 a fluorine-type coating material cured film containing magnesium fluoride or silicon dioxide, can be given.

 As a method of forming the low-refractive-index film on the high-refractive-index cured film obtained by curing the curable composition, when forming a metal oxide film, vacuum deposition, sputtering, and the like can be given. When
20 forming a fluorine-type coating material cured film, a method the same as the application (coating) method of the composition can be given.

 Reflection of light on the surface of the substrate can be effectively prevented by layering the high-refractive-index cured film and the low-refractive-index film on the substrate.

25 Since the laminate of the present invention has high hardness, low curling properties, excellent flexibility, low reflectance, and excellent chemical resistance, the laminate is particularly suitably used as an antireflective film for film-type liquid crystal elements, touch panels, plastic optical parts, and the like.

30 Examples

 The present invention is described below in detail by way of examples, which should not be construed as limiting the present invention.

 In the examples, "part" and "%" respectively refer to "part by weight" and "wt%" unless otherwise indicated.

35 In the present invention, "solid content" refers to the content of

components after removing volatile components such as a solvent from the composition. Specifically, the solid content refers to the content of a residue (nonvolatile components) obtained by drying the composition on a hot plate at 120°C for one hour.

5

Preparation Example 1: synthesis of specific organic compound

222 parts of isophorone diisocyanate was added dropwise to a solution of 221 parts of mercaptopropyltrimethoxysilane and 1 part of dibutyltin dilaurate in dry air at 50°C in one hour with stirring. The mixture was then stirred at 10 70°C for three hours. After the dropwise addition of 549 parts of NK Ester A-TMM-3LM-N (manufactured by Shin-Nakamura Chemical Co., Ltd.; consisting of 60 wt% of pentaerythritol triacylate and 40 wt% of pentaerythritol tetraacrylate; only pentaerythritol triacylate containing hydroxyl group takes part in the reaction) at 30°C in one hour, the mixture was stirred at 60°C for 10 hours to obtain an organic compound (Ab) containing 15 a polymerizable unsaturated group. The residual isocyanate content in the product analyzed by FT-IR was 0.1% or less. This indicates that the reaction completed almost quantitatively. In the infrared absorption spectrum of the product, the absorption peak at 2550 kayser characteristic of a mercapto group in the raw material and the absorption peak at 2260 kayser characteristic of the raw material isocyanate compound 20 disappeared, and the absorption peak at 1660 kayser characteristic of a urethane bond and an S(C=O)NH- group and the absorption peak at 1720 kayser characteristic of an acryloxy group appeared. This indicates that an acryloxy group-modified alkoxysilane containing an acryloxy group, S(C=O)NH- group, and urethane bond was produced. The above reaction yielded 773 parts of compounds shown by the formulas (3-1) and 25 (3-2). The product also contained 220 parts of pentaerythritol tetraacrylate which did not take part in the reaction.

Preparation Example 2: preparation of reactive particle liquid dispersion (A-1)

A mixture of 2.32 parts of the organic compound (Ab) containing a 30 polymerizable unsaturated group prepared in Preparation Example 1, 89.90 parts of a silica particle liquid dispersion (Aa) ("Methanol Silica Sol" manufactured by Nissan Chemical Industries, Ltd.) (silica content: 32%), 0.12 part of ion-exchanged water, and 0.01 part of p-hydroxyphenyl monomethyl ether was stirred at 60°C for four hours. After the addition of 1.36 parts of methyl orthoformate, the mixture was stirred at 60°C 35 for one hour to obtain reactive particles (liquid dispersion (A-1)). 2 g of the liquid

dispersion (A-1) was weighed on an aluminum dish and dried on a hot plate at 175°C for one hour. The dried product was weighed to indicate that the solid content was 30.7%. 2 g of the liquid dispersion (A-1) was weighed in a magnetic crucible, predried on a hot plate at 80°C for 30 minutes, and sintered at 750°C for one hour in a muffle
5 furnace. The inorganic content in the solid content was determined from the inorganic residue. As a result, the inorganic content was 90%.

Example 1

The reactive silica particles (A-1) and the dipentaerythritol
10 tetraacrylate (B-1) were mixed according to Table 1, and stirred at 40°C for two hours to obtain a homogenous solution. The solution was concentrated under reduced pressure using a rotary evaporator until the solid content became about 80%. Then, the remaining components shown in Table 1 were added to obtain a homogeneous composition solution. The solid content of the composition was 39.4%.

15 Compositions of Examples 2 to 7 and Comparative Examples 1 to 4 were obtained in the same manner as in Example 1 except for changing the components as shown in Table 1.

Evaluation of cured film

20 In order to demonstrate the effects of the composition of the present invention, a cured film obtained by applying, drying, and irradiating the composition was evaluated. The evaluation methods are described below. The evaluation results are shown in Table 1.

25 1. Preparation of evaluation cured film

(1) Substrate

A polycarbonate plate with dimensions of 50×100×2 mm was used.

(2) Conditions for application, drying, and curing

The composition was applied to the substrate by using a bar coater
30 so that the film thickness after drying was 6 µm under conditions of a pulling speed of 300 mm/min and an immersion time of 60 sec. The applied composition was dried in a hot blast oven at 80°C for three minutes. The dried product was irradiated at a dose of 1 J/cm² by using a conveyer-type mercury lamp, and allowed to stand at 25°C for 24 hours. The resulting product was then subjected to evaluation.

2. Evaluation method

(1) Repelling

The presence or absence of repelling due to local change in the thickness of the cured film was judged by naked eye observation. A case where repelling was not observed over the entire coating was evaluated as "good", a case where repelling was observed at one to three locations was evaluated as "fair", and a case where repelling was observed at four or more locations was evaluated as "bad". Repelling occurs during dip coating when the wettability between the coating of the composition and the substrate is insufficient.

10

(2) Thickness uniformity

The thickness of the coating at the center of the substrate and the thickness of the coating at the bottom were measured, and the difference (μm) was taken as the evaluation value. If the difference is 2 μm or less, the substrate may be suitably used as a substrate with a hard coating.

15

(3) Transparency

The transparency of the resulting cured film was judged by naked eye observation. A case where cloudiness was not observed was evaluated as "good", and case where cloudiness was observed was evaluated as "bad".

20

Table 1

[illegible]

F179: "Megafac F-179" manufactured by Dainippon Ink and Chemicals, Inc. Ltd.

F470: "Megafac F-470" manufactured by Dainippon Ink and Chemicals, Inc. Ltd.

EF351: "EFTOP EF-351" manufactured by Jemco Inc.

TR-701: polyoxyalkylene condensate of ethylenediamine, "TR-701" manufactured by

5 Asahi Denka Kogyo K.K.

B-1: dipentaerythritol tetraacrylate

E-1: 1-hydroxycyclohexyl phenyl ketone (Irgacure 184)

E-2: 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1 (Irgacure 907)

F-1: Irganox 1010; pentaerythrityltetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate]

10 F-2: Sanol LS-765; bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate

MIBK: Methyl isobutyl ketone

MEK: Methyl ethyl ketone

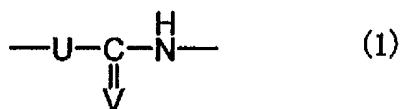
[Industrial Applicability]

The radiation-curable resin composition and the cured film are

15 suitable for use a material for a hard coating for an antireflective plate, a hard coating
for an optical sheet such for a touch panel, and a hard coating for a protective plate
used for a display of a mobile device such as a portable telephone, a protective coating
material to prevent stains or scratches on plastic optical parts, touch panels, film-type
liquid crystal elements, plastic containers, or flooring materials, wall materials, and
20 artificial marbles which are used for architectural interior finish; as an adhesive for
various substrates, a sealing material, and a vehicle for printing ink; and the like. Since
the radiation-curable resin composition of the present invention excels in uniform
applicability when applied by using a dip coating method, the radiation-curable resin
composition can be suitably use for a large display device such as a projection TV and
25 a small device such as a portable telephone.

CLAIMS

1. A radiation-curable resin composition, comprising: (A) particles produced by bonding oxide particles of at least one element selected from the group consisting of silicon, aluminum, zirconium, titanium, zinc, germanium, indium, tin, antimony, and cerium, with an organic compound including a polymerizable unsaturated group and a group shown by the following formula (1); (B) a compound containing two or more polymerizable unsaturated groups; (C) a surfactant containing a fluorine atom; and (D) an organic solvent containing one or more compounds selected from the group consisting of methanol, methyl isobutyl ketone, and n-butanol in an amount of 50 mass% or more in the total solvent.



- wherein U represents NH, O (oxygen atom), or S (sulfur atom), and V represents O or S.
2. The radiation-curable resin composition according to claim 1, wherein the organic compound contains a group shown by $[-\text{O}-\text{C}(=\text{O})-\text{NH}-]$ and at least one of groups shown by $[-\text{O}-\text{C}(=\text{S})-\text{NH}-]$ and $[-\text{S}-\text{C}(=\text{O})-\text{NH}-]$.
3. The radiation-curable resin composition according to claim 1 or 2, wherein the organic compound is a compound containing a silanol group or a compound which produces a silanol group by hydrolysis.
4. The radiation-curable resin composition according to any of claims 1 to 3,

wherein the surfactant (C) includes a fluorine-containing acrylic residue and a polydimethylsiloxane residue.

5. The radiation-curable resin composition according to any of claims 1 to 4,
wherein the component (D) is a mixture of methanol, methyl isobutyl ketone,
5 and n-butanol.
6. A cured film obtained by applying radiation to the radiation-curable resin
composition according to any of claims 1 to 5.
7. A laminate, comprising a transparent substrate and a layer of the cured film
according to claim 6.

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2005/000867

A. CLASSIFICATION OF SUBJECT MATTER
C09D4/00

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

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, 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 97/12942 A (DSM N.V; JAPAN SYNTHETIC RUBBER CO., LTD; JAPAN FINE COATINGS CO., LTD) 10 April 1997 (1997-04-10) cited in the application claims & JP 09 100111 A 15 April 1997 (1997-04-15) -----	1-7

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

☒ See patent family annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

21 March 2006

Date of mailing of the international search report

28/03/2006

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/NL2005/000867

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