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5-6-10, Tsukiji, Chuo-ku, Tokyo 104-8410 (JP). **TAN-ABE, Takayoshi** [JP/JP]; 5-6-10, Tsukiji, Chuo-ku, Tokyo 104-8410 (JP).

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(74) Agent: **VERWEIJ, P.D.**; DSM Intellectual Property, P.O. Box 9, NL-6160 MA Geleen (NL).

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(71) Applicants (*for all designated States except US*): **DSM IP ASSETS B.V.** [NL/NL]; Het Overloon 1, NL-6411 Te Heerlen (NL). **JSR CORPORATION** [JP/JP]; 5-6-10, Tsukiji Chuo-ku, Tokyo 104-8410 (JP). **JAPAN FINE COATINGS CO., LTD.** [JP/JP]; 57-1, Sawabe, Niihari-mura, Niihari-gun, Ibaraki 300-4104 (JP).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **SHINOHARA, Noriyasu** [JP/JP]; 5-6-10, Tsukiji, Chuo-ku, Tokyo 104-8410 (JP). **HATORI, Shin** [JP/JP]; 5-6-10, Tsukiji, Chuo-ku, Tokyo 104-8410 (JP). **USUI, Shinji** [JP/JP];

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(54) Title: CURABLE COMPOSITION CURED PRODUCT AND LAMINATE

(57) Abstract: To provide a curable composition having excellent applicability and capable of forming a coating (film) which has excellent hardness and flexibility on the surface of a substrate, and a cured film formed of the cured product of the composition. A curable composition comprising (A) 20 to 80 wt% of metal oxide particles having a refractive index of 1.50 or more to which an organic compound including a polymerizable unsaturated group is bonded, and (B) 10 to 70 wt% of a urethane (meth)acrylate compound having a polystyrene-reduced number average molecular weight of 750 or more in a gas permeation chromatography (GPC) pattern, the amount of each component being based on the total amount of the composition excluding a solvent, a cured product of the curable composition, and a laminate.



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CURABLE COMPOSITION, CURED PRODUCT, AND LAMINATE

The present invention relates to a curable composition, a cured product of the composition, and a laminate. More particularly, the present invention relates to a curable composition having excellent applicability and capable of forming a coating (film), which has a high refractive index and high hardness and exhibits excellent scratch resistance and excellent adhesion to an adjacent layer such as a substrate or a low-refractive-index layer, on the surface of a substrate (e.g. plastic (polycarbonate, polymethyl methacrylate, polystyrene, polyester, polyolefin, epoxy resin, melamine resin, triacetyl cellulose resin, ABS resin, AS resin, or norbornene resin), metal, wood, paper, glass, and slate), and to a hard coating cured film which exhibits excellent chemical resistance and flexibility.

A curable composition having excellent applicability and capable of forming a cured film, which exhibits excellent hardness, flexibility, scratch resistance, abrasion resistance, low curling properties (cured film showing a small degree of warping), adhesion, transparency, chemical resistance, and appearance, on a substrate has been demanded as a protective coating material for preventing scratches or stains on the surface of the substrate, an adhesive or a sealing material for a substrate, and a binder for printing ink.

A curable composition capable of forming a cured film which also has a high refractive index has been demanded for an antireflective film for a film-type liquid crystal element, touch panel, plastic optical parts, and the like.

Various compositions have been proposed in order to satisfy the above-described demands. However, a curable composition having excellent applicability and capable of forming a cured film which exhibits excellent hardness, flexibility, and low curling properties has not yet been obtained.

A technology of using a composition containing particles obtained by modifying the surface of colloidal silica having a refractive index of about 1.45 with a methacryloxysilane in combination with an acrylate as a radiation (photo) curable coating material has been proposed for a hard coating, for which a high refractive index is not required (Published Japanese Translation of PCT International Publication No. 58-500251). This type of radiation curable composition has been widely used due to excellent applicability and the like (Japanese Patent Application Laid-open No. 10-273595, Japanese Patent Application Laid-open No. 2000-143924, Japanese Patent Application Laid-open No. 2000-281863, Japanese Patent Application Laid-open No. 2000-49077, Japanese Patent Application Laid-open No. 2001-89535 and Japanese

Patent Application Laid-open No. 2001-200023).

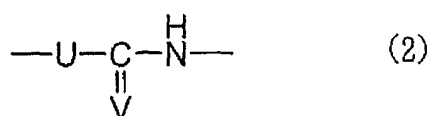
When layering a low-refractive-index film on a cured product of the related-art composition by application and using the resulting laminate as an antireflective film, although the antireflective effect is improved to some extent, the laminate does not exhibit satisfactory hardness and flexibility in combination.

When applying a hard coating material to a porous TAC film (substrate), the hard coating layer may become uneven. Specifically, if the (meth)acrylate compound used for the hard coating material has a low molecular weight, the (meth)acrylate compound permeates the TAC substrate so that the composition of the hard coating layer locally changes at the interface between the hard coating layer and the TAC substrate.

The present invention has been achieved in view of the above-described problems. The inventors of the present invention found that a composition having excellent applicability and capable of forming a coating (film), which exhibits high hardness and flexibility, on the surface of a substrate can be obtained by using a urethane (meth)acrylate compound having a high molecular weight. This finding has led to the completion of the present invention.

According to the present invention, the following curable composition, cured product, and laminate can be provided.

1. A curable composition comprising (A) 20 to 80 wt% of metal oxide particles having a refractive index of 1.50 or more to which an organic compound including a polymerizable unsaturated group is bonded, and (B) 10 to 70 wt% of a urethane (meth)acrylate compound having a polystyrene-reduced number average molecular weight of 750 or more in a gas permeation chromatography (GPC) pattern, the amount of each component being based on the total amount of the composition excluding a solvent.
2. The curable composition according to [1], wherein the organic compound in the component (A) includes a group shown by the following formula (2) in addition to the polymerizable unsaturated group,



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

represents O or S.

3. The curable composition according to [1] or [2], wherein the organic compound in the component (A) is a compound including a silanol group in the molecule or a compound which forms a silanol group by hydrolysis.
- 5 4. The curable composition according to any of [1] to [3], further comprising (C) 1 to 50 wt% of a (meth)acrylate compound other than the components (A) and (B) based on the total amount of the composition excluding a solvent.
5. The curable composition according to any of [1] to [4], further comprising (D) 0.01 to 10 wt% of a photoinitiator based on the total amount of the composition excluding a solvent.
- 10 6. The curable composition according to any of [1] to [5], wherein the content of the component (B) is 20 wt% or more for 100 wt% of the total (meth)acrylate component in the composition other than the component (A).
7. A cured film produced by curing the curable composition according to any of [1] to [6].
- 15 8. A laminate comprising the cured film according to [7].

According to the present invention, a curable composition having a high refractive index excellent applicability and capable of forming a coating (film), which has excellent hardness, scratch resistance, excellent flexibility, and high transparency, on the surface of a substrate, and a cured film formed of a cured product of the curable composition can be provided.

The curable composition, the cured product of the curable composition, and the laminate of the present invention are described below in detail.

#### 25 I. Curable composition

The curable composition of the present invention comprises (A) metal oxide particles having a refractive index of 1.50 or more to which an organic compound including a polymerizable unsaturated group is bonded, and (B) a urethane (meth)acrylate compound having a polystyrene-reduced number average molecular weight of 750 or more in a gas permeation chromatography (GPC) pattern.

Each component of the curable composition of the present invention is described below in detail.

1. Metal oxide particles (A) having refractive index of 1.50 or more to which organic compound including polymerizable unsaturated group

The component (A) used in the present invention is particles

prepared by bonding (Aa) metal oxide particles having a refractive index of 1.50 or more and (Ab) an organic compound including a polymerizable unsaturated group (hereinafter referred to as "reactive particles"). The metal oxide particles (Aa) and the organic compound (Ab) may be bonded through a covalent bond or a non-covalent  
5 bond such as by physical adsorption.

(1) Metal oxide particles (Aa)

The metal oxide particle (Aa) used in the present invention is preferably a metal oxide particle of at least one element selected from the group  
10 consisting of aluminum, zirconium, titanium, zinc, germanium, indium, tin, antimony, and cerium since such a particle has a high refractive index of 1.50 or more and the cured film of the resulting curable composition exhibits hardness and colorlessness. A metal oxide particle such as a silica particle containing silicon as the major component is not suitable for the present invention because the silica particle has a low refractive  
15 index of about 1.45.

As examples of the metal oxide particles (Aa), alumina particles, zirconia particles, titanium oxide particles, zinc oxide particles, germanium oxide particles, indium oxide particles, tin oxide particles, antimony-tin oxide (ATO) particles, indium-tin oxide (ITO) particles, antimony oxide particles, cerium oxide particles, and  
20 the like can be given. Of these, alumina particles, zirconia particles, and antimony oxide particles are preferable due to high hardness, with zirconia particles being particularly preferable. A cured coating with a high refractive index can be obtained by using oxide particles of zirconium, titanium, or the like. The cured coating can be provided with conductivity by using ATO particles, or the like. These particles may be  
25 used either individually or in combination of two or more. The oxide particles (Aa) are preferably either in the form of powder or dispersed in a liquid. If the oxide particles are dispersed in a liquid, the dispersion medium is preferably an organic solvent from the viewpoint of miscibility and dispersibility with other components. As examples of such an organic solvent, alcohols such as methanol, ethanol, isopropanol, butanol, and  
30 octanol; ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone; esters such as ethyl acetate, butyl acetate, ethyl lactate,  $\gamma$ -butyrolactone, propylene glycol monomethyl ether acetate, and propylene glycol monoethyl ether acetate; ethers such as ethylene glycol monomethyl ether and diethylene glycol monobutyl ether; aromatic hydrocarbons such as benzene, toluene,  
35 and xylene; amides such as dimethylformamide, dimethylacetamide, and N-methylpyrrolidone; and the like can be given. Of these, methanol, isopropanol, butanol,

methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate, butyl acetate, toluene, and xylene are preferable.

The number average particle diameter of the metal oxide particles (Aa) measured by electron microscopy is preferably 0.001 to 2  $\mu\text{m}$ , still more preferably 0.001 to 0.2  $\mu\text{m}$ , and particularly preferably 0.001 to 0.1  $\mu\text{m}$ . If the number average particle diameter exceeds 2  $\mu\text{m}$ , the transparency of the cured product may decrease or the surface condition of the resulting film may be impaired. Various surfactants and amines may be added in order to improve dispersibility of the particles.

As commercially available products of zirconia particles, EP, UEP, RC (manufactured by Daiichi Kigenso Kagaku Kogyo Co., Ltd.), N-PC, PCS (manufactured by Nippon Denko Co., Ltd.), TZ-3Y-E, TZ-4YS, TZ-6YS, TZ-8YS, TZ-10YS, TZ-0 (manufactured by Tosoh Corporation), and the like can be given.

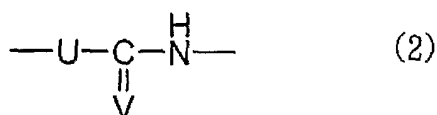
An aqueous dispersion product of alumina is commercially available as Alumina Sol-100, -200, -520 (manufactured by Nissan Chemical Industries, Ltd.); an isopropanol dispersion product of alumina is commercially available as AS-150I (manufactured by Sumitomo Osaka Cement Co., Ltd.); an toluene dispersion product of alumina is commercially available as AS-150T (manufactured by Sumitomo Osaka Cement Co., Ltd.); a toluene dispersion product of zirconia is commercially available as HXU-110JC (manufactured by Sumitomo Osaka Cement Co., Ltd.); an aqueous dispersion product of zinc antimonate powder is commercially available as Celnax (manufactured by Nissan Chemical Industries, Ltd.); powder or solvent dispersion products of alumina titanium oxide, tin oxide, indium oxide, zinc oxide, etc., are commercially available as NanoTek (manufactured by C.I. Kasei Co., Ltd.); an aqueous dispersion sol of antimony doped-tin oxide is commercially available as SN-100D (manufactured by Ishihara Sangyo Kaisha, Ltd.); ITO powder is commercially available as a product manufactured by 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 metal oxide particle (Aa) may be globular, hollow, porous, rod-like, plate-like, fibrous, or amorphous. The shape of the metal oxide particle (Aa) is preferably globular. The specific surface area of the metal oxide particle (Aa) determined by a BET method using nitrogen is preferably 10 to 1000  $\text{m}^2/\text{g}$ , still more preferably 50 to 500  $\text{m}^2/\text{g}$ , and particularly preferably 50 to 200  $\text{m}^2/\text{g}$ . The metal oxide particles (Aa) may be used either in the form of dry powder or dispersed in water or in an organic solvent. For example, a metal oxide fine particle liquid dispersion known in the art may be used as the liquid dispersion. Use of a metal oxide particle

liquid dispersion is particularly preferable when excellent transparency is required for the resulting cured product.

## (2) Organic compound (Ab)

5                   The organic compound (Ab) used in the present invention is a compound including a polymerizable unsaturated group. The organic compound (Ab) is preferably an organic compound including a group shown by the following formula (2). The organic compound (Ab) preferably includes a group [-O-C(=O)-NH-], and further includes at least one of groups [-O-C(=S)-NH-] and [-S-C(=O)-NH-]. The organic  
10                   compound (Ab) is preferably either a compound including a silanol group in the molecule or a compound which forms a silanol group by hydrolysis.



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

### (i) Polymerizable unsaturated group

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

25                   The polymerizable unsaturated group is a structural unit which undergoes addition polymerization by active radicals.

### (ii) Group shown by formula (2)

30                   As specific examples of the group [-U-C(=V)-NH-] shown by the formula (2) included in the organic compound, [-O-C(=O)-NH-], [-O-C(=S)-NH-], [-S-C(=O)-NH-], [-NH-C(=O)-NH-], [-NH-C(=S)-NH-], or [-S-C(=S)-NH-] can be given. These groups may be used either individually or in combination of two or more. Use of the group [-O-C(=O)-NH-] and at least one of the groups [-O-C(=S)-NH-] and [-S-C(=O)-NH-] in combination is preferable from the viewpoint of thermal stability.

The group  $[-U-C(=V)-NH-]$  shown by the formula (2) may generate a moderate cohesive force between the molecules due to hydrogen bonds, and provide the cured product with excellent mechanical strength, adhesion to a substrate or to an adjacent layer such as a high-refractive-index layer, heat resistance, and the like.

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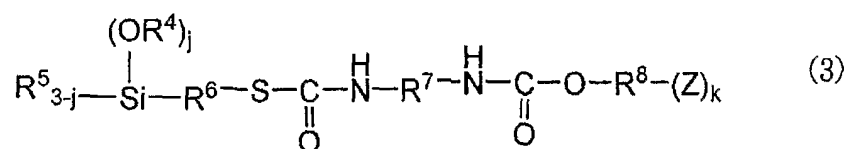
(iii) Silanol group or group which forms silanol group by hydrolysis

The organic compound (Ab) is preferably a compound including either a silanol group in the molecule or a compound which forms a silanol group by hydrolysis. As the compound which forms a silanol group, a compound in which an  
10 alkoxy group, aryloxy group, acetoxyl group, amino group, halogen atom, or the like is bonded to a silicon atom can be given. Of these, a compound in which an alkoxy group or an aryloxy group is bonded to a silicon atom, specifically, a compound including an alkoxysilyl group or a compound including an aryloxysilyl group is preferable.

The silanol group or the silanol group-forming site of the silanol  
15 group-forming compound is a structural unit which bonds to the oxide particles (Aa) by condensation or condensation that occurs after hydrolysis.

(iv) Preferable embodiment

As a preferable example of the organic compound (Ab), a compound  
20 shown by the following formula (3) can be given.



wherein  $R^4$  and  $R^5$  may individually represent a hydrogen atom or an alkyl group or aryl  
25 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.  $j$  is an integer from 1 to 3.

As examples of the group shown by  $[(R^4O)_jR^5_{3-j}Si-]$ , a trimethoxysilyl  
group, triethoxysilyl group, triphenoxysilyl group, methyldimethoxysilyl group,  
dimethylmethoxysilyl group, and the like can be given. Of these, a trimethoxysilyl  
30 group or a triethoxysilyl group is preferable.

$R^6$  represents a divalent organic group having an aliphatic or an aromatic structure having 1 to 12 carbon atoms, and may include a linear, branched, or cyclic structure. As examples of such an organic group, methylene, ethylene,

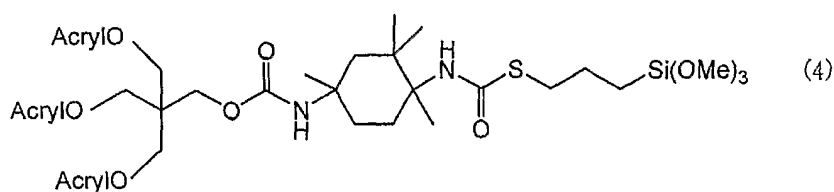
propylene, butylene, hexamethylene, cyclohexylene, phenylene, xylylene, dodecamethylene, and the like can be given.

$R^7$  represents a divalent organic group, which is generally selected from divalent organic groups having a molecular weight of 14 to 10,000, and preferably 76 to 500. As examples of such divalent organic groups, a linear polyalkylene group such as hexamethylene, octamethylene, and dodecamethylene; an alicyclic or polycyclic divalent organic group such as cyclohexylene and norbornylene; a divalent aromatic group such as phenylene, naphthylene, biphenylene, and polyphenylene; and an alkyl-substituted or aryl-substituted product of these groups can be given. These divalent organic groups may include an atomic group having an element other than a carbon atom and a hydrogen atom. These divalent organic groups may include a polyether bond, polyester bond, polyamide bond, or polycarbonate bond.

$R^8$  represents an organic group with a valence of  $(k+1)$ , and is preferably selected from the group consisting of linear, branched, or cyclic saturated and unsaturated hydrocarbon groups.

Z represents a monovalent organic group which has a polymerizable unsaturated group in the molecule, and undergoes an intermolecular crosslinking reaction in the presence of active radicals. k represents an integer preferably from 1 to 20, more preferably from 1 to 10, and particularly preferably from 1 to 5.

As specific examples of the compound shown by the formula (3), a compound shown by the following formula (4) can be given.



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

The organic compound (Ab) used in the present invention may be synthesized by a method described in Japanese Patent Application Laid-open No. 9-100111, for example. In this method, mercaptopropyltrimethoxysilane and isophorone diisocyanate are mixed in the presence of dibutyltin dilaurate in dry air. After allowing the mixture to react at 60 to 70°C for several hours, pentaerythritol triacrylate is added to the mixture. The resulting mixture is allowed to react at 60 to 70°C for several hours to prepare the organic compound (Ab).

### (3). Reactive particles (A)

The organic compound (Ab) including a silanol group or a group which forms a silanol group by hydrolysis is mixed with the metal oxide particles (Aa) and hydrolyzed to bond the organic compound (Ab) and the metal oxide particles (A). The amount of the organic polymer component, that is, the hydrolyzate and condensate of the hydrolyzable silane, in the resulting reactive particles (A) may be determined by thermogravimetric analysis as the constant weight loss (%) when completely burning a dry powder at room temperature to 800°C in air.

The amount of the 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) (metal oxide particles (Aa) and organic compound (Ab) in total). If the amount of the organic compound (Ab) bonded to the metal oxide particles (Aa) is less than 0.01 wt%, dispersibility of the reactive particles (A) in the composition may be insufficient, whereby transparency and scratch resistance of the cured product may become insufficient. The amount of the metal oxide particles (Aa) in the raw materials for the reactive particles (A) is preferably 5 to 99 wt%, and still more preferably 10 to 98 wt%.

The amount (content) of the reactive particles (A) in the curable composition is preferably 20 to 80 wt%, and still more preferably 30 to 50 wt% for 100 wt% of the total amount of the composition excluding an organic solvent (total amount of the components (A), (B), (C), and (D)). If the amount is less than 20 wt%, the cured film may exhibit insufficient hardness or a cured film with a high refractive index may not be obtained. If the amount exceeds 80 wt%, film formability of the composition may be insufficient. In this case, the content of the oxide particles (Aa) forming the reactive particles (A) is preferably 65 to 95 wt% of the reactive particles (A). 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) does not include the amount of dispersion medium.

2. Urethane (meth)acrylate compound (B) having polystyrene-reduced number average molecular weight of 750 or more in gas permeation chromatography (GPC) pattern (hereinafter referred to as "high-molecular-weight urethane (meth)acrylate compound (B)")

The high-molecular-weight urethane (meth)acrylate compound (B) is a urethane (meth)acrylate compound having a polystyrene-reduced number average

molecular weight of 750 or more in a gas permeation chromatography (GPC) pattern.

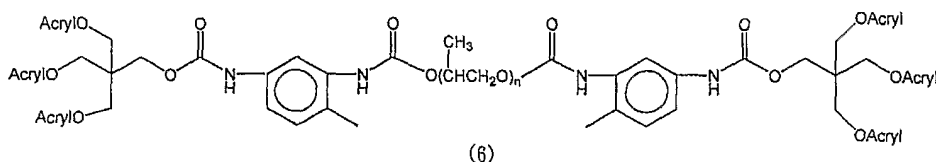
Generally, a urethane (meth)acrylate compound is a mixture of several types of compounds having different molecular weights. The component (B) is the component having a polystyrene-reduced number average molecular weight of 750 or more included in such a urethane (meth)acrylate compound. The content of the component (B) in such a mixture is determined by multiplying the total amount of the mixture by the area ratio of components with a polystyrene-reduced number average molecular weight of 750 or more to components with a polystyrene-reduced number average molecular weight of less than 750 in the gas permeation chromatography (GPC) pattern.

The high-molecular-weight urethane (meth)acrylate compound (B) has a function of increasing the flexibility of the cured product obtained using the compound (B).

The high-molecular-weight urethane (meth)acrylate compound (B) may include two or more, and preferably six or more (meth)acryloyl groups. The molecular weight per each (meth)acryloyl group is preferably 1000 or less, and still more preferably 700 or less.

The GPC pattern of the high-molecular-weight urethane (meth)acrylate compound (B) is measured by using an HLC-8020 type high-speed liquid chromatography system (manufactured by Tosoh Corporation). A styrene-divinylbenzene copolymer resin is used as a GPC column, and tetrahydrofuran is used for an eluant.

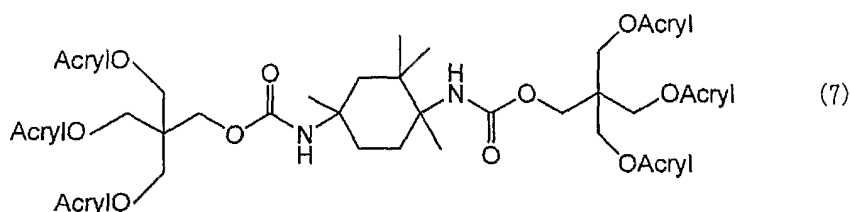
The high-molecular-weight urethane (meth)acrylate compound (B) is not particularly limited insofar as the compound has the above-described properties. As specific examples of the compound (B), compounds shown by the following formulas (6) and (7) can be given.



wherein "Acryl" represents an acryloyl group,  $n$  represents an integer from 10 to 50, and preferably from 20 to 40.

The compound shown by the formula (6) may be synthesized by mixing 2,4-tolylene diisocyanate with polypropylene glycol in the presence of di- $n$ -butyltin dilaurate, allowing the mixture to react at room temperature to 30°C for several

hours, adding pentaerythritol triacrylate to the resulting product, and further allowing the mixture to react at 50 to 70°C for three to six hours.



5

wherein "Acryl" represents an acryloyl group.

The compound shown by the formula (7) may be obtained by mixing isophorone diisocyanate with pentaerythritol triacrylate in the presence of dibutyltin dilaurate, and allowing the mixture to react at 50 to 70°C for four to eight hours.

10

Commercially available products may also be used as the high-molecular-weight urethane (meth)acrylate compound (B). As specific examples of such products, HDP-M20, UN-3320HA, HDP-4M (manufactured by Negami Chemical Industrial Co., Ltd.), and the like can be given.

15

The content of the high-molecular-weight urethane (meth)acrylate compound (B) used in the present invention is preferably 10 to 70 wt%, and still more preferably 30 to 70 wt% for 100 wt% of the total amount of the composition excluding an organic solvent (total amount of the components (A), (B), (C), and (D)). If the amount is in the range of 10 to 70 wt%, the resulting cured film exhibits good flexibility.

20

The content of the compound (B) is preferably 40 wt% or more, still more preferably 80 wt% or more, and particularly preferably 100 wt% for 100 wt% of the total (meth)acrylate component in the composition other than the component (A). If the content of the compound (B) is 40 wt% or more, warping of the resulting cured film can effectively be reduced. The total (meth)acrylate component other than the component (A) refers to the (meth)acrylate component contained in the total soluble components excluding the component (A) (insoluble particles). Specifically, the total (meth)acrylate component refers to the total amount of the component (B) and a component (C) described below.

25

3. (Meth)acrylate compound (C) other than components (A) and (B)

30

A polyfunctional (meth)acrylate compound (C) other than the components (A) and (B) may be added to the composition of the present invention

insofar as the effect of the present invention is not impaired.

The polyfunctional (meth)acrylate compound is suitably used to improve the curability and hardness of the resulting cured film. The "polyfunctional (meth)acrylate compound" herein refers to two or more (meth)acryloyl groups in one molecule. As the polyfunctional (meth)acrylate compound (C), a (meth)acrylate compound including three or more (meth)acryloyl groups is preferable, and a (meth)acrylate compound including five or more (meth)acryloyl groups is more preferable in view of film formability and hardness of the cured film.

As preferred examples of the polyfunctional (meth)acrylate compound (C), pentaerythritol triacrylate, dipentaerythritol hexacrylate, dipentaerythritol pentacrylate, and the like can be given.

As commercially available products of the polyfunctional (meth)acrylate compound, Kayarad DPHA, PET-30 (manufactured by Nippon Kayaku Co., Ltd.), Aronix M-305, M-400, M-402, M-404 (manufactured by Toagosei Co., Ltd.), NK Ester A-TMM-3LM-N (manufactured by Shin-Nakamura Chemical Co., Ltd.), and the like can be given.

The content of the compound (C) used in the present invention is preferably 1 to 50 wt%, and still more preferably 1 to 20 wt% for 100 wt% of the total amount of the composition excluding an organic solvent (total amount of the components (A), (B), (C), and (D)). If the content of the compound (C) is 20 wt% or more, the resulting cured film may exhibit poor flexibility and a high degree of curling.

#### 4. Radical polymerization initiator (D)

The composition of the present invention may optionally include a radical polymerization initiator (D).

As examples of the radical polymerization initiator (D), a compound which thermally generates active radicals (heat polymerization initiator), a compound which generates active radicals by applying radiation (light) (radiation (photo) polymerization initiator), and the like can be given.

There are no specific limitations to the radiation (photo) polymerization initiator insofar as an initiator decomposes upon irradiation and generates radicals to initiate polymerization. Examples of the initiator include acetophenone, acetophenone benzyl ketal, 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-1,2-diphenylethan-1-one, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3-methylacetophenone, 4-chlorobenzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diaminobenzophenone,

benzoin propyl ether, benzoin ethyl ether, benzyl dimethyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 2-hydroxy-2-methyl-1-phenylpropan-1-one, thioxanethone, diethylthioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1,4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl)ketone, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide, and oligo(2-hydroxy-2-methyl-1-(4-(1-methylvinyl)phenyl)propanone).

As examples of commercially available products of the radiation (photo) polymerization initiator, Irgacure 184, 369, 651, 500, 819, 907, 784, 2959, CGI1700, CGI1750, CGI1850, CG24-61, Darocur 1116, 1173 (manufactured by Ciba Specialty Chemicals K.K.), Lucirin TPO (manufactured by BASF), Ebecryl P36 (manufactured by UCB), Esacure KIP150, KIP65LT, KIP100F, KT37, KT55, KTO46, KIP75/B (manufactured by Lamberti), and the like can be given.

The amount of the radical polymerization initiator (D), which is optionally used in the composition of the present invention, is preferably 0.01 to 10 wt%, and still more preferably 0.1 to 5 wt% for 100 wt% of the composition (total amount of the components (A) to (D)). If the amount is less than 0.01 wt%, the hardness of the cured product may be insufficient. If the amount exceeds 10 wt%, the inside (lower layer) of the cured product may remain uncured.

The composition of the present invention may be cured using a photoinitiator and a heat polymerization initiator in combination.

As preferred examples of the heat polymerization initiator, peroxides and azo compounds can be given. Specific examples include benzoyl peroxide, t-butyl peroxybenzoate, and azobisisobutyronitrile.

#### 5. Organic solvent (E)

The composition of the present invention includes an organic solvent. The composition may be diluted with an organic solvent (E) in order to adjust the thickness of the resulting coating. When the composition is used for an antireflective film or as a coating material, the viscosity of the composition is usually 0.1 to 50,000 mPa·s/25°C, and preferably 0.5 to 10,000 mPa·s/25°C.

There are no specific limitations to the organic solvent (E). As examples of the organic solvent (E), alcohols such as methanol, ethanol, isopropanol, butanol, and octanol; ketones such as acetone, methyl ethyl ketone (MEK), methyl

isobutyl ketone, and cyclohexanone; esters such as ethyl acetate, butyl acetate, ethyl lactate,  $\gamma$ -butyrolactone, propylene glycol monomethyl ether acetate, and propylene glycol monoethyl ether acetate; ethers such as ethylene glycol monomethyl ether and diethylene glycol monobutyl ether; aromatic hydrocarbons such as benzene, toluene, and xylene; amides such as dimethylformamide, dimethylacetamide, and N-methylpyrrolidone; and the like can be given. Of these, a high boiling point solvent such as methyl isobutyl ketone, cyclohexanone, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, toluene, or xylene is preferable.

The amount of the organic solvent (E) used in the composition of the present invention is usually 30 to 80 wt%, and preferably 50 to 80 wt% of the total amount of the composition. If the amount is in the range of 30 to 80 wt%, the resulting composition exhibits good applicability.

#### 6. Other components

The curable composition of the present invention may optionally include additives such as a photosensitizer, polymerization inhibitor, polymerization adjuvant, leveling agent, wettability improver, surfactant, plasticizer, UV absorber, antioxidant, antistatic agent, inorganic filler, pigment, and dye insofar as the effect of the present invention is not impaired.

#### 7. Preparation of composition

The composition of the present invention is prepared as follows. A reaction vessel equipped with a stirrer is charged with the reactive particle liquid dispersion (component (A)), the high-molecular-weight urethane (meth)acrylate compound (component (B)), and optionally the radiation (photo) polymerization initiator (component (D)), the polyfunctional (meth)acrylate (component (C)), and the organic solvent (component (E)). The mixture is stirred at 35°C to 45°C for two hours to prepare a composition of the present invention.

When the solvent ( $\alpha$ ) used in the first reactive particle liquid dispersion is replaced with a solvent ( $\beta$ ), the amount of the solvent ( $\beta$ ) added must be 1.3 times of the amount of the solvent ( $\alpha$ ) in the reactive particle liquid dispersion, and the mixture is stirred under the same condition. Subsequently, the mixture is concentrated under vacuum using a rotary evaporator until the amount of the mixture becomes equal to the amount before adding the solvent ( $\beta$ ) to the mixture.

## 8. Application (coating) of composition

The composition of the present invention is suitable for a hard coating, an antireflective film, or a coating material. As examples of a substrate to which the composition is applied, plastic (polycarbonate, polymethacrylate, polystyrene, polyester, polyolefin, epoxy resin, melamine resin, triacetyl cellulose resin, ABS resin, AS resin, norbornene resin, etc.), metal, wood, paper, glass, slate, and the like can be given. The substrate may be in the shape of a plate, a film, or a three-dimensional formed product. As the coating method, a typical coating method such as dipping, spray coating, flow coating, shower coating, roll coating, spin coating, brush coating, and the like can be given. The thickness of the coating after drying and curing is 0.1 to 400  $\mu\text{m}$ , and preferably 1 to 200  $\mu\text{m}$ .

## 9. Curing of composition

The curable composition of the present invention is cured by heating and/or radiation (light). When the composition is cured by heating, an electric heater, infrared lamp, hot blast, and the like may be used as the heat source. When the composition is cured by applying radiation (light), there are no specific limitations to the radiation source insofar as the composition can be cured in a short time after application. As examples of the source of infrared rays, a lamp, resistance heating plate, laser, and the like can be given. As examples of the source of visible rays, sunlight, a lamp, fluorescent lamp, laser, and the like can be given. As examples of 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 utilizing thermoelectrons generated from a commercially available tungsten filament, a cold cathode method which generates electron beams by applying a high voltage pulse through a metal, and a secondary electron method which utilizes secondary electrons generated by collision between ionized gaseous molecules and a metal electrode can be given. As examples of the source of  $\alpha$ -rays,  $\beta$ -rays, and  $\gamma$ -rays, fissionable substances such as  $\text{Co}^{60}$  and the like can be given. As the source of  $\gamma$ -rays, a vacuum tube which causes accelerated electrons to collide with an anode or the like may be utilized. Either one type or a combination of two or more types of radiation may be used. In the latter case, two or more types of radiation may be applied either simultaneously or at specific intervals.

The composition of the present invention may be cured in air, or under anaerobic conditions such as in nitrogen. The cured product exhibits excellent scratch resistance even when the composition is cured under anaerobic condition.

## II. Cured film

The cured film of the present invention may be obtained by applying the curable composition to a substrate such as a plastic substrate, and curing the composition. Specifically, the composition is applied to a substrate, volatile components of the composition are preferably dried at 0 to 200°C, and the composition is cured by heating and/or radiation to obtain a coating formed product. When curing the composition by heating, the composition may preferably be cured at 20 to 150°C for 10 seconds to 24 hours. When curing the composition by applying radiation, ultraviolet rays or electron beams may preferably be used. In this case, the dose of ultraviolet rays is preferably 0.01 to 10 J/cm<sup>2</sup>, and still more preferably 0.1 to 2 J/cm<sup>2</sup>. Electron beams are preferably applied at an accelerated voltage of 10 to 300 KV, an electron density of 0.02 to 0.30 mA/cm<sup>2</sup>, and a dose of 1 to 10 Mrad.

Since the cured film of the present invention has high hardness and excellent flexibility, and is capable of forming a coating (film) which has excellent scratch resistance, and adhesion to a substrate and to an adjacent layer of the substrate or a low-refractive-index layer, the cured film is particularly suitable as an antireflective film for film-type liquid crystal element, touch panel, plastic optical parts, and the like.

## III. Laminate

The cured film of the present invention is usually laminated on a substrate as a hard coating layer, and a high-refractive-index layer or a low-refractive-index layer may further be laminated on the hard coating layer to form a laminate which is suitable as an antireflective film. The antireflective film may include layers other than the layers described above. For example, combinations of a high-refractive-index film and a low-refractive-index film may be laminated on the antireflective film to form a wide-band antireflective film having relatively uniform reflectance properties to light over a wide wavelength range. The antireflective film may also include an antistatic layer.

There are no specific limitations to the substrate used in the present invention. However, if the laminate is used as an antireflective film, substrates made of plastic (polycarbonate, polymethylmethacrylate, polystyrene, polyester, polyolefin, epoxy resin, melamine resin, triacetyl cellulose (TAC) resin, ABS resin, AS resin, norbornene resin, and the like) can be used.

As examples of the high-refractive-index film used in the present invention, a metal oxide particle-containing (e.g. zirconia particle) coating material

cured film having a refractive index of 1.65 to 2.20, and the like can be given.

As examples of the low-refractive-index film used in the present invention, a metal oxide film made of magnesium fluoride or silicon dioxide, a fluorine-type coating material cured film, and the like, each of which has a refractive index of 1.38 to 1.45, can be given. The fluorine-type coating material cured film may include fine particles having high hardness to improve scratch resistance of the film. As specific examples of the fine particles having high hardness, silica particles, and the like may be preferable so that the refractive index of a low refractive-index layer may remain unchanged. The shape of the silica particle is not particularly limited. The shape of the silica particle may be hollow, or porous, which is a structure having numerous air spaces. The silica particles having these shapes may maintain a refractive index lower.

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

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

The laminate of the present invention is particularly suitable as an antireflective film for film-type liquid crystal elements, touch panels, plastic optical parts, and the like, since the laminate has excellent scratch resistance, a low reflectance, and excellent chemical resistance.

## Examples

Examples of the present invention are described below in detail. However, the scope of the present invention is not limited to the following examples. In the examples, "part(s)" refers to "part(s) by weight" and "%" refers to "wt%" unless otherwise indicated.

### Preparation Example 1: preparation of zirconia sol (Aa)

300 parts of spherical zirconia fine powder (UEP-100: manufactured by Daiichi Kigenso Kagaku Kogyo Co., Ltd., primary particle size: 10 to 30 nm) was added to 700 parts of methyl ethyl ketone, and dispersed for 168 hours using glass beads. The glass beads were then removed to obtain 950 parts of methyl ethyl ketone zirconia sol (Aa). 2 g of the dispersion sol was weighed in an aluminum dish and dried

on a hot plate at 120°C for one hour. The dried product was weighed to indicate that the solid content was 30%.

Preparation Example 2: preparation of organic compound (Ab) including polymerizable unsaturated group

222 parts of isophorone diisocyanate was added dropwise with stirring at 50°C in one hour to a solution of 221 parts of mercaptopropyltrimethoxysilane and one part of dibutyltin dilaurate in dry air. The mixture was stirred at 70°C for three hours. After the addition of 549 parts of NK Ester A-TMM-3LM-N (manufactured by Shin-Nakamura Chemical Co., Ltd.) (60 wt% of pentaerythritol triacrylate and 40 wt% of pentaerythritol tetraacrylate; only pentaerythritol triacrylate including a hydroxyl group takes part in reaction) dropwise at 30°C in one hour, the mixture was heated at 60°C with stirring for 10 hours to obtain an organic compound (Ab) including a polymerizable unsaturated group. The residual isocyanate content in the resulting product was analyzed using FT-IR and found to be 0.1% or less. This indicates that the reaction was completed almost quantitatively. In the infrared absorption spectrum of the product, the absorption peak at 2550 kayser characteristic to a mercapto group and the absorption peak at 2260 kayser characteristic to an isocyanate group in the raw material disappeared, and the absorption peak at 1660 kayser characteristic to a urethane bond and S(C=O)-NH- group and the absorption peak at 1720 kayser characteristic to an acryloyl group appeared. This indicates that an acryloyl group-modified alkoxysilane including an acryloyl group and an -S(C=O)-NH- group as polymerizable unsaturated groups and having a urethane bond was produced. 773 parts of the compound (Ab) shown by the formula (4) was thus obtained. The resulting product also contained 220 parts of pentaerythritol tetraacrylate which had not taken part in the reaction.

Preparation Example 3: preparation of urethane (meth)acrylate (compound shown by formula (7))

A vessel equipped with a stirrer was charged with a solution of 18.8 parts of isophorone diisocyanate and 0.2 parts of dibutyltin dilaurate. After the dropwise addition of 93 parts of NK Ester A-TMM-3LM-N (manufactured by Shin-Nakamura Chemical Co., Ltd) (only pentaerythritol triacrylate having hydroxyl group takes part in the reaction) at 10°C for one hour the mixture was stirred at 60°C for six hours to obtain a reaction solution.

The residual isocyanate content in the reaction solution measured by

FT-IR in the same manner as in Preparation Example 2 was 0.1 wt% or less. This indicates that the reaction was completed almost quantitatively. It was also found that a urethane bond and an acryloyl group (polymerizable unsaturated group) were included in the molecule.

- 5                      75 parts of the compound shown by the formula (7) was thus obtained. The reaction solution also contained 37 parts of pentaerythritol tetraacrylate which had not taken part in the reaction.

Preparation Example 4: preparation of reactive zirconia sol (A-1)

- 10                      A mixed solution of 1.16 parts of a mixture of the organic compound (Ab) including a polymerizable unsaturated group prepared in Preparation Example 2 and pentaerythritol tetraacrylate, 237 parts of the toluene zirconia sol (Aa) (zirconia content: 30%) prepared in Preparation Example 1, 0.1 part of ion-exchanged water, and 0.03 parts of p-hydroxyphenyl monomethyl ether was stirred at 60°C for three  
15 hours. After the addition of 1.0 part of methyl orthoformate, the mixture was heated and stirred at 60°C for one hour to obtain reactive particles (liquid dispersion (A-1)). 2 g of the liquid dispersion (A-1) was weighed in an aluminum dish and dried on a hot plate at 120°C for one hour. The dried product was weighed to confirm that the solid content was 31%. 2 g of the liquid dispersion (A-1) was weighed in a magnetic crucible,  
20 predried on a hot plate at 80°C for 30 minutes, and sintered at 750°C for one hour in a muffle furnace. The inorganic content in the solid content was determined from the resulting inorganic residue. As a result, the inorganic content was 93%.

Preparation Example 5: preparation of compound shown by formula (6)

- 25                      A reaction vessel equipped with a stirrer was charged with 10.23 wt% of 2,4-tolylene diisocyanate, 0.08 wt% of di-n-butyltin dilaurate, 0.02 wt% of 2,6-di-t-butyl-p-cresol, and 0.01 wt% of phenothiazine. Then, 59.43 wt% of polypropylene glycol having an average molecular weight of 2000 was added dropwise to the mixture with stirring while maintaining the solution temperature at 30°C or lower. After the  
30 addition, the mixture was allowed to react at 30°C for two hours. After the addition of 30.23 wt% of pentaerythritol triacrylate, the mixture was allowed to react at 50 to 70°C for four hours. The reaction was terminated when the residual isocyanate content became 0.1 wt% or less. The resulting product was measured by GPC. As a result, the area ratio of components with a polystyrene-reduced number average molecular weight of 750 or more to components with a polystyrene-reduced number average molecular  
35 weight of less than 750 was 5.9 (referred to as "high molecular weight/low molecular

weight" in Table 1).

### Example 1

#### (1) Preparation of curable composition

5                   126.1 parts of the reactive zirconia sol (liquid dispersion (A-1))  
(reactive zirconia particles: 39.1 parts) prepared in Preparation Example 4, 54.20 parts  
of the compound shown by the formula (6), 1.2 parts of the compound shown by the  
formula (7), 0.8 parts of pentaerythritol tetraacrylate, and 230.6 parts of methyl ethyl  
ketone (MEK) were stirred in a UV-shielded container at 30°C for two hours to obtain a  
10 homogeneous composition solution. The pentaerythritol tetraacrylate was the  
pentaerythritol tetraacrylate contained in the organic compound (Ab) and the  
compound shown by the formula (7). The solid content of the composition measured in  
the same manner as in Preparation Example 1 was 30%.

#### (2) Preparation of cured film

15                   The composition obtained in (1) was applied to a TAC film using a  
wire bar coater (#60) for a desired film thickness and dried at 80°C for one minute in an  
oven to form a coating. The coating was cured by applying UV rays in air at a dose of  
0.3 J/cm<sup>2</sup> using a high-pressure mercury lamp to obtain the TAC film with a high-  
20 refractive-index film having a thickness of 15 to 18 µm. The flexibility of the resulting  
cured film was evaluated. The results are shown in Table 1.

### Examples 2 to 4 and Comparative Example 1

25                   Curable compositions and cured films of Examples 2 to 4 and  
Comparative Example 1 were prepared in the same manner as in Example 1 except for  
using the compounds shown in Table 1 instead of the compound shown by the formula  
(6). The flexibility of the resulting cured films was evaluated. The results are shown in  
Table 1.

30                   A specimen with a size of 10×1 cm was cut from the obtained TAC  
film on which the cured film was formed, and was wound around a metal rod. The  
flexibility of the cured film was evaluated by the minimum diameter of the metal rod at  
which cracks were not observed with the naked eye.

Table 1

| Component (parts by weight)                                 | GPC area ratio<br>(high molecular<br>weight/ low molecular<br>weight) | Example   |       |       |       | Comparative<br>Example |
|-------------------------------------------------------------|-----------------------------------------------------------------------|-----------|-------|-------|-------|------------------------|
|                                                             |                                                                       | 1         | 2     | 3     | 4     |                        |
| Reactive zirconia particles (A-1)                           |                                                                       | 45.77     | 45.77 | 45.77 | 45.77 | 45.77                  |
| Compound shown by formula (6)                               | 5.9                                                                   | 54.20     | -     | -     | -     | -                      |
| HDP-4M                                                      | 6.1                                                                   | -         | 54.20 | -     | -     | -                      |
| HDP-M20                                                     | 4.0                                                                   | -         | -     | 54.20 | -     | -                      |
| UN-3320HA                                                   | 1.5                                                                   | -         | -     | -     | 54.20 | -                      |
| Pentaerythritol triacrylate                                 |                                                                       | -         | -     | -     | -     | 54.20                  |
| Pentaerythritol tetraacrylate                               |                                                                       | 0.80      | 0.80  | 0.80  | 0.80  | 0.80                   |
| Compound shown by formula (7)                               |                                                                       | 1.20      | 1.20  | 1.20  | 1.20  | 1.20                   |
| Irgacure 184                                                |                                                                       | 5.00      | 5.00  | 5.00  | 5.00  | 5.00                   |
| MEK                                                         |                                                                       |           |       |       |       |                        |
| Solid content (wt%)                                         |                                                                       | 30.0      | 30.0  | 30.0  | 30.0  | 30.0                   |
| <Flexibility evaluation of cured product>                   |                                                                       |           |       |       |       |                        |
| Minimum diameter (mm)<br>(film thickness: 15 to 18 $\mu$ m) |                                                                       | 4 or less | 7     | 12    | 12    | 16                     |

In Table 1, the amount of the reactive zirconia particles (A-1) indicates the weight of the dry fine powder (excluding the organic solvent).

The meanings of the abbreviations in Table 1 are as follows.

Reactive zirconia particles (A-1): reactive zirconia particles prepared in Preparation

5 Example 4

Zirconia particles (Aa): zirconia sol prepared in Preparation Example 1

Compound shown by formula (6): high-molecular-weight urethane (meth)acrylate compound prepared in Preparation Example 5

10 HDP-4M: high-molecular-weight urethane (meth)acrylate manufactured by Negami Chemical Industrial Co., Ltd. (number of functional groups: 15; solid content: 70 wt% (solvent: methyl ethyl ketone); molecular weight: 50,000 to 300,000)

HDP-M20: high-molecular-weight urethane (meth)acrylate manufactured by Negami Chemical Industrial Co., Ltd. (number of functional groups: 10; solid content: 80 wt% (solvent: methyl ethyl ketone); molecular weight: 4900)

15 UN-3220HA: high-molecular-weight urethane (meth)acrylate manufactured by Negami Chemical Industrial Co., Ltd. (number of functional groups: 6; solid content: 100 wt% (solvent: methyl ethyl ketone); molecular weight: 1500)

The GPC area ratios (high molecular weight/low molecular weight) of HDP-4M, HDP-M20, UN-3220HA, and PET-30 are shown in Table 1.

20 Irgacure 184: 1-hydroxycyclohexyl phenyl ketone (photoinitiator, manufactured by Ciba Specialty Chemicals K.K.)

MEK: methyl ethyl ketone

As shown in Table 1, the cured films of the examples exhibit excellent flexibility. On the contrary, the cured film of Comparative Example 1, which does not  
25 include the high-molecular-weight (meth)acrylate compound (component (B)), exhibits poor flexibility.

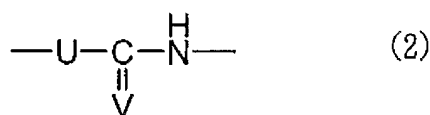
The curable composition and the cured product of the present invention are suitably used for a protective coating material for preventing scratches or stains on plastic optical parts, touch panels, film-type liquid crystal elements, plastic  
30 containers, and flooring materials, wall materials, and artificial marble used as an architectural interior finish; an antireflective film for film-type liquid crystal elements, touch panels, or plastic optical parts; an adhesive or a sealing material for various substrates; a binder for printing ink; and the like. The curable composition and the cured product can be particularly suitably used for an antireflective film.

35 The curable composition and the cured product of the present invention are useful for an optical material which requires a high refractive index, such

as a high-refractive-index antireflective film material, and a lens material. The curable composition and the cured product of the present invention are particularly suitable for applications for which flexibility is required.

CLAIMS

1. A curable composition comprising (A) 20 to 80 wt% of metal oxide particles having a refractive index of 1.50 or more to which an organic compound including a polymerizable unsaturated group is bonded, and (B) 10 to 70 wt% of a urethane (meth)acrylate compound having a polystyrene-reduced number average molecular weight of 750 or more in a gas permeation chromatography (GPC) pattern, the amount of each component being based on the total amount of the composition excluding a solvent.
2. The curable composition according to claim 1, wherein the organic compound in the component (A) includes a group shown by the following formula (2) in addition to the polymerizable unsaturated group,



15

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

3. The curable composition according to claim 1 or 2, wherein the organic compound in the component (A) is a compound including a silanol group in the molecule or a compound which forms a silanol group by hydrolysis.
4. The curable composition according to any of claims 1 to 3, further comprising (C) 1 to 50 wt% of a (meth)acrylate compound other than the components (A) and (B) based on the total amount of the composition excluding a solvent.
5. The curable composition according to any of claims 1 to 4, further comprising (D) 0.01 to 10 wt% of a photoinitiator based on the total amount of the composition excluding a solvent.
6. The curable composition according to any of claims 1 to 5, wherein the content of the component (B) is 20 wt% or more for 100 wt% of the total (meth)acrylate component in the composition other than the component (A).
7. A cured film produced by curing the curable composition according to any of claims 1 to 6.
8. A laminate comprising the cured film according to claim 7.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/NL2005/000869

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| <b>A. CLASSIFICATION OF SUBJECT MATTER</b><br>G03F7/027 C08K3/22 G02B1/10 C08G18/80 C08G18/81<br>C09D175/16                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                                |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| According to International Patent Classification (IPC) or to both national classification and IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                                |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| <b>B. FIELDS SEARCHED</b><br>Minimum documentation searched (classification system followed by classification symbols)<br>C08K G03F G02B C08G                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                                |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                                |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| Electronic data base consulted during the international search (name of data base and, where practical, search terms used)<br>EPO-Internal, WPI Data, PAJ                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                                |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                                |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| Category*                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | Relevant to claim No.                                                                                                          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | US 2002/058737 A1 (NISHIWAKI ET AL)<br>16 May 2002 (2002-05-16)<br>paragraph '0013! - paragraph '0116!<br>paragraph '0148! - paragraph '0154!<br>paragraph '0198! - paragraph '0200!;<br>claims 1-22                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | 1-8                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | US 2003/065050 A1 (YAMAGUCHI ET AL)<br>3 April 2003 (2003-04-03)<br>cited in the application<br>paragraph '0005! - paragraph '0063!<br>paragraph '0079! - paragraph '0082!;<br>claims 1-5; examples 1,2                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | 1-8                                                                                                                            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | WO 03/080749 A (DSM/JSR)<br>2 October 2003 (2003-10-02)<br>page 3, line 3 - page 8, line 13<br>page 10, line 11 - line 36; claims 1,2;<br>example 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 1                                                                                                                              |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| <input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                                |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| * Special categories of cited documents :                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                                |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; border: none;">           *A* document defining the general state of the art which is not considered to be of particular relevance<br/>           *E* earlier document but published on or after the international filing date<br/>           *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)<br/>           *O* document referring to an oral disclosure, use, exhibition or other means<br/>           *P* document published prior to the international filing date but later than the priority date claimed         </td> <td style="width: 50%; vertical-align: top; border: none;">           *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<br/>           *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<br/>           *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.<br/>           *&amp;* document member of the same patent family         </td> </tr> </table> |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                                                                                                                | *A* document defining the general state of the art which is not considered to be of particular relevance<br>*E* earlier document but published on or after the international filing date<br>*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)<br>*O* document referring to an oral disclosure, use, exhibition or other means<br>*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<br>*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<br>*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.<br>*&* document member of the same patent family |
| *A* document defining the general state of the art which is not considered to be of particular relevance<br>*E* earlier document but published on or after the international filing date<br>*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)<br>*O* document referring to an oral disclosure, use, exhibition or other means<br>*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<br>*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<br>*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.<br>*&* document member of the same patent family |                                                                                                                                |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| Date of the actual completion of the international search<br><br><div style="text-align: center; font-weight: bold;">6 March 2006</div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | Date of mailing of the international search report<br><br><div style="text-align: center; font-weight: bold;">13/03/2006</div> |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | Authorized officer<br><br><div style="text-align: center; font-weight: bold;">Bourgonje, A</div>                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)                                           | Publication<br>date                                  |
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