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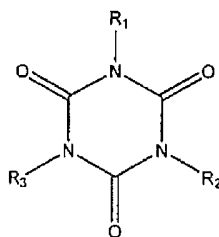
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(54) Title: CURABLE COMPOSITION CONTAINING CONDUCTIVE PARTICLES, CURED PRODUCT OF THE CURABLE COMPOSITION, AND LAMINATE



(1)

(57) Abstract: To provide a curable composition exhibiting excellent applicability and capable of forming a coating that provides antistatic properties on the surface of a substrate and exhibits excellent scratch resistance, and a cured film including a cured product of the composition. A curable composition, comprising: (A) 5 to 50 wt% of zinc antimonate particles, and (B) 10 to 50 wt% of a compound shown by the following Formula (1), the amount of each component being based on the total amount of the composition excluding a solvent; a cured product obtained by curing the composition; and a laminate of the cured product.

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CURABLE COMPOSITION CONTAINING CONDUCTIVE PARTICLES, CURED
PRODUCT OF THE CURABLE COMPOSITION, AND LAMINATE

The present invention relates to a curable composition containing
5 conductive particles, a cured product of the curable composition, and a laminate. More particularly, the present invention relates to a curable composition containing conductive particles, which exhibits excellent applicability and is capable of forming a coating (film) having excellent scratch resistance and excellent adhesion to a substrate or an adjacent layer on the surface of a substrate (such as plastic (polycarbonate,
10 polymethyl methacrylate, polystyrene, polyester, polyolefin, epoxy resin, melamine resin, triacetyl cellulose resin, ABS resin, AS resin, or norbornene resin), metal, wood, paper, glass, or slate), and to a cured film (hard coating) for a printer belt or a printer drum.

A curable composition having excellent applicability and capable of
15 forming a cured film which exhibits excellent hardness, flexibility, scratch resistance, abrasion resistance, and adhesion on the surface of a substrate has been demanded as a protective coating material for preventing scratches or stains on the surface of a substrate; an adhesive or a sealing material for a substrate; and a binder for printing ink.

20 A printer belt is a transfer belt or feed belt used as a component of an image forming device such as a laser printer or an ink-jet printer, and is formed by using a polycarbonate resin or a fluoro resin material containing an antistatic agent. Since the printer belt repeatedly rubs against other components or paper, it is necessary to improve the scratch resistance of the printer belt in order to increase the
25 life. A printer drum is a photosensitive drum or a transfer drum used as a component of an image forming device such as a laser printer. The photosensitive drum has a structure in which a photoconductive coating layer having a thickness of about several tens of μm is provided over the outer circumference of a cylinder made of aluminum or the like. The transfer drum is formed by using a resin material the same as the material
30 for the transfer belt. Since the printer drum also repeatedly rubs against other components or paper, it is necessary to improve the scratch resistance of the printer drum in order to increase the life.

As a laser printing method, an intermediate transfer belt method in which an electrostatic latent image is formed on a photosensitive drum or a
35 photosensitive belt, and a toner image obtained by developing the electrostatic latent image using toner is transferred onto a transfer belt, a transfer drum method in which

an electrostatic latent image is formed on a photosensitive drum and a toner image is transferred onto a transfer drum, a tandem method in which photosensitive drums are provided in units of basic colors of a color printer, and the like have been known.

However, the printer belt and the printer drum used in these methods also suffer from
5 the above-described problem.

Japanese Patent Application Laid-open No. 10-231444 discloses an antistatic hard coating resin composition having transparency with a haze value of 1.5 or less, which is obtained by dispersing zinc antimonate sol in a UV-curable (meth)acrylate containing at least one (meth)acryloyl group in the molecule using a
10 dispersant. The patent document 1 describes a substrate provided with excellent abrasion resistance, transparency, and antistatic properties by curing the composition.

Japanese Patent Application Laid-open No. 2004-141732 discloses a cured product of a composition which contains a compound having an isocyanurate ring structure and does not contain particles. In the patent document 2, hardness is
15 provided by increasing the film thickness. In addition, this composition does not contain conductive particles.

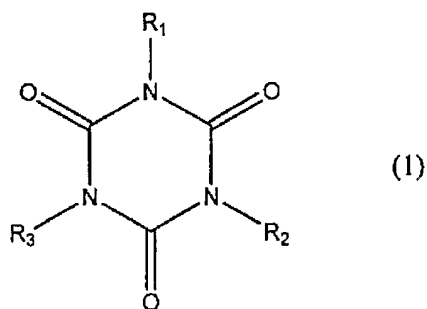
The antistatic hard coating resin composition disclosed in the patent document 1 can improve scratch resistance. However, the composition exhibits insufficient scratch resistance when used as a hard coating material for a printer belt or
20 a printer drum which is repeatedly subjected to frictional contact.

The present invention has been achieved in view of the above-described problems. An object of the present invention is to provide a curable composition having excellent applicability and capable of forming a coating (film) which exhibits antistatic properties and excellent scratch resistance on the surface of a
25 substrate, a cured product of the curable composition (particularly a hard coating for a printer belt or a printer drum), and a laminate including the cured product.

The inventors of the present invention have conducted extensive studies in order to achieve the above object. As a result, the inventors have found that antistatic properties and excellent scratch resistance can be obtained by using a resin
30 component mainly containing an isocyanurate (meth)acrylate compound and zinc antimonate particles as conductive particles instead of antimony-doped tin oxide (ATO) particles, which are widely used as a conductivity providing material and require a larger amount to be added than zinc antimonate particles. This finding has led to the completion of the present invention.

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

1. A curable composition, comprising: (A) 5 to 50 wt% of zinc antimonate particles, and (B) 10 to 50 wt% of a compound shown by the following formula (1),



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wherein R^1 , R^2 , and R^3 individually represent monovalent organic groups, with at least two of R^1 , R^2 , and R^3 being $-R^4OCOCR^5=CH_2$, R^4 represents a divalent organic group having 2 to 8 carbon atoms, and R^5 represents a hydrogen atom or a methyl group; the amount of each component being based on the total amount of the composition excluding a solvent.

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2. The curable composition according to [1], wherein the component (B) is tris((meth)acryloxyethyl) isocyanurate.
3. The curable composition according to [1] or [2], further comprising (C) 10 to 70 wt% of a polyfunctional (meth)acrylate compound other than the components (A) and (B) based on the total amount of the composition excluding a solvent.
4. The curable composition according to any of [1] to [3], wherein the composition containing the component (B) in an amount of 20 wt% or more for 100 wt% of the total (meth)acrylate component in the composition excluding the component (A).
5. A cured film produced by curing the curable composition according to any of [1] to [4].
6. The cured film according to [5], the cured film being a hard coating film for a printer belt.
7. The cured film according to [5], the cured film being a hard coating film for a printer drum.
8. A laminate comprising the cured product according to [5].

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According to the present invention, a curable composition exhibiting

excellent applicability and capable of forming a coating (film) which exhibits excellent antistatic properties and excellent scratch resistance on the surface of a substrate, and a cured film formed of a cured product of the composition can be provided.

According to the present invention, since a hard coating layer having
5 antistatic properties and scratch resistance can be formed on the surface of a printer belt or a printer drum which is repeatedly subjected to frictional contact, the life of the printer belt or the printer drum can be increased.

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

I. Curable composition

The curable composition of the present invention includes (A) zinc antimonate particles, and (B) a compound shown by the formula (1).

15 The components of the curable composition of the present invention are described below in detail.

1. Zinc antimonate particles (A)

The component (A) used in the present invention is zinc antimonate
20 particles.

(1) Zinc antimonate particles (A)

The zinc antimonate particles (A) used in the present invention are added as a component which provides electrical conductivity and improves scratch
25 resistance of the resulting cured film.

The number average particle diameter of the zinc antimonate particles (A) determined by a dynamic light scattering method is preferably 10 to 100 nm, and still more preferably 10 to 30 nm. If the particle diameter is 10 to 100 nm, the resulting cured product exhibits excellent scratch resistance.

30 It is preferable that the zinc antimonate particles (A) be in the form of powder or dispersed in a liquid. When using the zinc antimonate particles (A) dispersed in a liquid, the dispersion medium is preferably an organic solvent from the viewpoint of miscibility with other components and dispersibility of the particles. As examples of the organic solvent, alcohols such as methanol, ethanol, isopropanol, butanol, and octanol; ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, and
35 cyclohexanone; esters such as ethyl acetate, butyl acetate, ethyl lactate, γ -

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. In particular, methanol, isopropanol, butanol, methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate, butyl acetate, toluene, and xylene are preferable.

In the present invention, a commercially available product may be used as zinc antimonate particles. As specific examples of such products, Celnax CX-Z210IP (double oxide sol ($\text{ZnO-Sb}_2\text{O}_5$) obtained by combining zinc oxide (ZnO) and antimony pentoxide (Sb_2O_5); oxide concentration: 20.9 wt%; dispersion medium: isopropanol; number average particle diameter: 158 nm; manufactured by Nissan Chemical Industries, Ltd.), CX-Z300H, CX-Z300H-F, CX-Z401M, CX-Z401M-F, CX-Z403M, CX-Z403M-F, CX-Z410M, CX-Z410M-F, CX-Z210IP-F, and the like can be given.

The shape of the zinc antimonate particle is not particularly limited. However, it is preferable that the shape of the zinc antimonate particle be globular, hollow, porous, rod, plate, fibrous, or amorphous. The zinc antimonate particle is preferably globular. The specific surface area of the zinc antimonate particle (A) (determined by BET method using nitrogen) is preferably 10 to 1000 m^2/g , and still more preferably 100 to 500 m^2/g . The zinc antimonate particles (A) may be used in the form of dry powder or dispersed in water or an organic solvent. For example, a dispersion liquid of fine metal zinc antimonate particles known in the art may be used. In applications in which excellent transparency is required for the resulting cured product, it is preferable to use a dispersion liquid of the zinc antimonate particles.

The amount (content) of the zinc antimonate particles (A) used in the curable composition is preferably 5 to 50 wt%, and still more preferably 5 to 20 wt% for 100 wt% of the total amount of the composition excluding an organic solvent (total amount of components (A), (B), and (C)). If the amount the zinc antimonate particles is 5 to 50 wt%, the composition exhibits excellent scratch resistance.

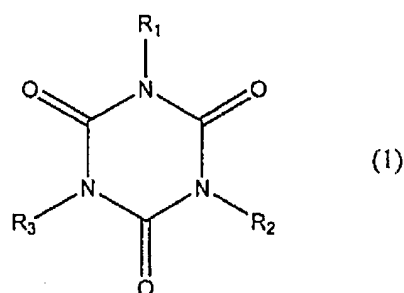
2. Compound (B) shown by formula (1)

The component (B) used in the present invention reduces curling of the resulting cured product and provides of the resulting cured product with flexibility while maintaining hardness. Moreover, the component (B) improves the steel wool scratch resistance of a laminate including the resulting cured product and a specific

low-refractive-index layer.

The compound (B) shown by the following formula (1), which is the component (B) used in the present invention, is an isocyanuric acid derivative containing a polymerizable unsaturated group.

5



wherein R^1 , R^2 , and R^3 individually represent monovalent organic groups, with at least two of R^1 , R^2 , and R^3 being $-R^4OCOCR^5=CH_2$, R^4 represents a divalent organic group having 2 to 8 carbon atoms, and R^5 represents a hydrogen atom or a methyl group.

The component (B) preferably contains two or more polymerizable unsaturated groups in the molecule. The polymerizable unsaturated group is not particularly limited. The polymerizable unsaturated group is preferably a (meth)acrylate group. If the component (B) contains two or more polymerizable unsaturated groups, the crosslink density is increased so that a decrease in hardness can be reduced.

As specific examples of the component (B) which may be used in the present invention, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, tris(2-hydroxyethyl)isocyanurate di(meth)acrylate, tris(2-hydroxyethyl)isocyanurate mono(meth)acrylate, bis(2-hydroxyethyl)isocyanurate di(meth)acrylate, bis(2-hydroxyethyl)isocyanurate mono(meth)acrylate, (meth)acrylate of ethylene oxide (EO), propylene oxide, or caprolactam addition product of the starting alcohol of these compounds, and the like can be given. Of these, isocyanuric acid EO modified tri(meth)acrylate is particularly preferable.

As commercially available products which may be preferably used as the compound (B), Aronix M-313, M-315, M-325, M-326, M-327 (manufactured by Toagosei Co., Ltd.), SR-368 (manufactured by Sartomer Company), and the like can be given. The above compounds may be used either individually or in combination of two or more.

The compound (B) is used in the present invention in an amount of preferably 10 to 50 wt%, still more preferably 20 to 50 wt%, and particularly preferably

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35 to 50 wt% for 100 wt% of the total amount of the composition excluding an organic solvent (total amount of components (A), (B), and (C)). If the amount is less than 10 wt%, the resulting cured film may be curled. If the amount exceeds 50 wt%, the resulting cured film may exhibit insufficient hardness.

5 The amount of the compound (B) is preferably 20 wt% or more, still more preferably 40 wt% or more, and particularly preferably 60 wt% or more for 100 wt% of the total (meth)acrylate component in the composition of the present invention excluding the component (A). If the amount is 20 wt% or more, the resulting cured film can effectively be prevented from warping. The total (meth)acrylate component
10 excluding the component (A) used herein refers to the (meth)acrylate component included in the total soluble component excluding the component (A) (insoluble particles).

 Specifically, the total (meth)acrylate component refers to the total amount of the components (B) and (C) (component (C) is described later).

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

 The compound (C) is preferably used to improve the flexibility of the resulting cured film.

 The polyfunctional (meth)acrylate compound as the component (C) is
20 a (meth)acrylate monomer containing two or more polymerizable unsaturated groups in the molecule. The polyfunctional (meth)acrylate compound is preferably used to improve the curability and hardness of the resulting cured film. The expression "polyfunctional" used herein means that the (meth)acrylate compound contains two or more (meth)acryloyl groups in the molecule. From the viewpoint of film formability and
25 hardness, a tri- or higher functional (meth)acrylate compound is preferable, with a penta- or higher functional (meth)acrylate compound being still more preferable.

 As preferable examples of the polyfunctional (meth)acrylate compound, pentaerythritol triacrylate, dipentaerythritol hexaacrylate, dipentaerythritol pentaacrylate, and the like can be given.

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 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.

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 The component (C) is used in the present invention in an amount of preferably 10 to 70 wt%, and still more preferably 20 to 60 wt% for 100 wt% of the total

amount of the composition excluding an organic solvent (total amount of components (A), (B), and (C)). If the amount exceeds 70 wt%, the resulting cured film may exhibit insufficient flexibility and anti-curling properties. If the amount is less than 10 wt%, the resulting cured film may exhibit insufficient hardness.

5

4. Radical polymerization initiator (D)

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

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

There are no specific limitations to the radiation (photo) polymerization initiator insofar as the initiator decomposes and generates radicals upon
 15 irradiation to initiate polymerization. Examples of the radiation (photo) polymerization 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,
 20 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-
 25 (2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl)ketone, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide, oligo(2-hydroxy-2-methyl-1-(4-(1-methylvinyl)phenyl)propanone), and the like.

As commercially available products of the radiation (photo) polymerization initiator, Irgacure 184, 369, 651, 500, 819, 907, 784, 2959, CGI1700, CGI1750, CGI1850, CG24-61, Darocure 1116, 1173 (manufactured by Ciba Specialty Chemicals Inc.), 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.

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The radical polymerization initiator (D), which is used in the present invention as an optional component, is used in an amount of preferably 0.01 to 10 wt%,

and still more preferably 0.1 to 5 wt% for 100 wt% of the total amount of the composition excluding an organic solvent (total amount of components (A) to (D)). If the amount is less than 0.01 wt%, the resulting cured product may exhibit insufficient hardness. If the amount exceeds 10 wt%, the inside (lower layer) of the cured product
5 may remain uncured.

When curing the composition of the present invention, a photoinitiator and a heat polymerization initiator may optionally be used in combination.

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

5. Organic solvent (E)

The composition of the present invention may be diluted with (E) an organic solvent in order to adjust the thickness of a coating formed by using the
15 composition. For example, when the composition is used as an antireflective film or 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). However, since the compound used as the component (B) has high crystallinity, it is preferable to
20 use a high-boiling solvent so that the composition of the present invention is uniformly applied. As specific 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, γ -butyrolactone, propylene glycol monomethyl
25 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, high-boiling solvents such as methyl isobutyl ketone, cyclohexanone, propylene glycol
30 monomethyl ether acetate, propylene glycol monoethyl ether acetate, toluene, and xylene are preferable.

The organic solvent (E) is used in the composition of the present invention in an amount of usually 30 to 80 wt%, and preferably 40 to 80 wt% of the total amount of the composition. If the amount of the organic solvent (E) is 30 to 80 wt%, the
35 composition exhibits excellent applicability.

6. Other component (F)

The curable composition of the present invention may include a photosensitizer, polymerization inhibitor, polymerization adjuvant, leveling agent, wettability improver, surfactant, plasticizer, UV absorber, antioxidant, antistatic agent, inorganic filler, pigment, dye, or the like insofar as the effects of the present invention are not impaired.

7. Preparation of composition

The composition of the present invention is prepared as follows.

10 A reaction vessel equipped with a stirrer is charged with a zinc antimonate particle dispersion liquid (component (A)), a radiation (photo)polymerization initiator (component (D)), a compound shown by the formula (1) (component (B)), a polyfunctional (meth)acrylate (component (C)), and a urethane (meth)acrylate (component (C)). The mixture is stirred at 35° to 45°C for two hours to obtain the

15 composition of the present invention.

When replacing the solvent with a solvent (β) differing from a solvent (α) used in the zinc antimonate particle dispersion liquid, the solvent (β) is also added to the mixture in an amount 1.3 times the amount of the solvent (α) of the zinc antimonate particle dispersion liquid, and the mixture is stirred under the same

20 conditions. Then, the composition solution is concentrated under reduced pressure by using a rotary evaporator until the weight before adding the solvent (β) is reached to obtain the composition of the present invention.

8. Application (coating) of composition

25 The curable composition of the present invention is preferably used as a hard coating or a coating material, and particularly useful as a hard coating material for a laser printer belt or a printer drum. As examples of the substrate to be coated, plastic (e.g. polycarbonate, polymethacrylate, polystyrene, polyester, polyolefin, epoxy, melamine, triacetyl cellulose, ABS, acrylonitrile-styrene resin, and norbornene resin), metal, wood, paper, glass, slate, and the like can be given. As a

30 material for a printer drum or transfer drum (i.e. substrate to be coated), a thermoplastic resin material may preferably be used. As examples of the thermoplastic resin material, polyvinylidene fluoride, polyethylene, polypropylene, polymethylpentene-1, polystyrene, polyamide, polysulfone, polyarylate, polyethylene terephthalate,

35 polyphenylene sulfide, polyethersulfone, polyether nitrile, thermoplastic polyimide material, polyether ether ketone, thermotropic liquid crystal polymer, polyamide acid,

polycarbonate, and polymethyl methacrylate, a mixed resin of these resins, and a thermoplastic elastomer formed by using the mixed resin can be given. As a surface material for a photosensitive drum (i.e. substrate to be coated), cadmium sulphide, a selenium compound, polysilane, or the like may preferably be used.

5 The substrate may be in the shape of a plate, a film, or a three-dimensional formed product. As the coating method, an ordinary coating method such as dipping, spray coating, flow coating, shower coating, roll coating, spin coating, or brush coating can be given. The thickness of the coating after drying and curing is usually 0.1 to 400 μm , and preferably 1 to 200 μm .

10

9. Curing of composition

 The curable composition of the present invention may be cured by applying heat and/or radiation (light). When curing the composition by applying heat, an electric heater, infrared lamp, hot blast, or the like may be used as the heat source.

15 When curing the composition by applying radiation (light), there are no specific limitations to the radiation source insofar as the composition can be cured in a short period of 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
20 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
25 generated by collision between ionized gaseous molecules and a metal electrode can be given. As examples of the sources of α -rays, β -rays, and γ -rays, fissionable substances such as Co^{60} and the like can be given. As the source of α -rays, a vacuum tube which causes accelerated electrons to collide with an anode or the like may be utilized. The radiation may be used either individually or in combination of two or more
30 types. In the latter case, two or more types of radiation may be applied either simultaneously or at certain intervals of time.

 The curing reaction of the composition of the present invention may be carried out in air or under anaerobic conditions such as in a nitrogen atmosphere. Even when the composition of the present invention is cured under anaerobic
35 conditions, the resulting cured product exhibits excellent scratch resistance.

II. Cured film

A 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 applied composition. In more detail, the composition is applied to the substrate, and volatile components are dried at a temperature of preferably 0° to 200°C. Then, the composition is cured by applying heat and/or radiation as described above to obtain a coating formed product. When curing the composition by applying heat, the composition is preferably cured at 20° to 150°C for 10 seconds to 24 hours. When curing the composition by applying radiation, it is preferable to use ultraviolet rays or electron beams. In this case, the dose of the ultraviolet rays is preferably 0.01 to 10 J/cm², and still more preferably 0.1 to 2 J/cm². Electron beams are preferably applied at an accelerating voltage of 10 to 300 KV, an electron density of 0.02 to 0.30 mA/cm², and a dose of 1 to 10 Mrad.

Since the cured film of the present invention can form a coating (film) having antistatic properties and exhibiting excellent scratch resistance and excellent adhesion to a substrate or an adjacent layer, the cured film is particularly suitable for applications that require antistatic properties such as a hard coating for a laser printer belt or printer drum.

III. Laminate

The cured film of the present invention is usually laminated on a substrate as a hard coating layer. The cured film is suitably used for applications that require antistatic properties and scratch resistance, particularly as a hard coating for a laser printer belt or printer drum. The printer belt is a transfer (resin) belt 1 shown in FIG. 1 or an adhesion transfer (resin) belt 21 shown in FIG. 4. The printer drum is a photosensitive drum shown in FIGS. 1 to 3 or a transfer drum shown in FIG. 2.

The laminate of the present invention formed by curing the curable composition of the present invention by applying ultraviolet rays exhibits excellent scratch resistance. Moreover, since the component (B) (isocyanuric acid derivative containing a polymerizable unsaturated group) contains a cyclic structure and has crystallinity, hardness is not decreased, whereby the laminate or cured film of the present invention exhibits excellent scratch resistance.

Furthermore, adhesion to the substrate and scratch resistance are improved by adding the component (B) (isocyanuric acid derivative containing a polymerizable unsaturated group).

Examples

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

Preparation Example 1

1. Synthesis of silicone compound (F-1)

A reaction vessel was charged with 80 parts of α -[3-(2'-hydroxymethoxy)propyl]polymethylsiloxane ("FM0411" manufactured by Dow Corning Toray Silicone Co., Ltd.). After the addition of 1 part or less of 2,6-di-t-butylcresol, 1 part or less of phenothiazine, and 10 parts of 2,4-diisocyanatotoluene as polymerization inhibitors, the solution temperature was maintained at 15° to 25°C. After the addition of 1 part of dibutyltin dilaurate as a catalyst, the solution temperature was increased to 35° to 45°C. After allowing the mixture to react for one hour, 10 parts of 2-hydroxyethyl acetate was added, and the solution temperature was maintained at 50° to 60°C. After two hours, the isocyanate content was measured and found to be 0.1 part or less to obtain a target reactive silicone. [0048]

Example 1

A reaction vessel equipped with a stirrer was charged with 43.638 parts of zinc antimonate particle dispersion liquid (zinc antimonate double oxide, "Celnax CX-Z210IP" manufactured by Nissan Chemical Industries, Ltd.; dispersion medium: isopropanol; solid content: 21 wt%) (9.164 parts as zinc antimonate particles), 83.714 parts of methyl ethyl ketone, and 139.640 parts of methyl isobutyl ketone, and the mixture was stirred. After the addition of 34.463 parts of tris(2-hydroxyethyl)isocyanurate acrylate ("Aronix M-315" manufactured by Toagosei Co., Ltd.), 51.875 parts of dipentaerythritol hexaacrylate, 2.177 parts of 1-hydroxycyclohexyl phenyl ketone (photoinitiator, "Irgacure 184" manufactured by Ciba Specialty Chemicals Inc.), 2.177 parts of 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one (photoinitiator, "Irgacure 907" manufactured by Ciba Specialty Chemicals Inc.), 0.009 parts of methoxyphenol (polymerization inhibitor manufactured by Wako Pure Chemical Industries, Ltd.), and 0.136 parts of the silicone compound (F-1) prepared in Preparation Example 1, the mixture was stirred at room temperature for 60 minutes to obtain a homogeneous composition. 2 g of the composition was weighed on an aluminum dish and dried at 175°C for one hour on a hot plate. The dried product was

weighed to indicate that the solid content was 27.9%.

Example 2 and Comparative Examples 1 and 2

A curable composition was obtained in the same manner as in
5 Example 1 except for using the components shown in Table 1.

Preparation of cured film

The curable composition was applied to an adhesive PET substrate
("A4300" manufactured by Toyobo Co., Ltd.) by using an applicator bar (#20) for each
10 example shown in Table 1. The curable composition was applied so that the thickness
after curing was 6 μm . The PET substrate was placed in an oven at 80°C for three
minutes to dry the curable composition. Then, ultraviolet rays were applied to the
curable composition by using a UV conveyer. The illuminance of the ultraviolet rays
was 900 mJ/cm^2 .

15

Properties of cured film

(1) Surface resistivity (ohm/square)

The surface resistivity (ohm/square) of the cured film was measured
at an applied voltage of 100 V by using a high-resistance meter ("Agilent 4339B"
20 manufactured by Agilent Technologies, Inc.) and a resistivity cell ("16008B"
manufactured by Agilent Technologies, Inc.). The results are shown in Table 1.

(2) Scratch resistance

A Gakusin type abrasion tester ("AB-301" manufactured by Tester
25 Sangyo Co, Ltd.) was provided with steel wool ("Bonstar No. 0000" manufactured by
Nihon Steel Wool Co. Ltd.). The surface of the cured film was scratched 10 times at a
load of 500 g/cm^2 to confirm the presence or absence of scratches on the surface of
the cured film with the naked eye. A cured film in which occurrence of removal or
scratches was not observed or observed only to a small extent was evaluated as
30 "Good", and a cured film in which a part of the cured film was removed or streak-
shaped scratches occurred on the surface of the cured film was evaluated as "Bad".

- 15 -

Table 1

Composition (wt%)	Example		Comparative Example	
	1	2	1	2
Zinc antimonate particles (solid content)	9.164	9.164	-	38.627
ATO	-	-	9.164	-
Tris(2-hydroxyethyl)isocyanurate acrylate	34.463	34.463	34.463	-
Dipentaerythritol hexaacrylate	51.875	51.875	51.875	52.188
1-Hydroxycyclohexyl phenyl ketone	2.177	2.177	2.177	4.485
2-Methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one	2.177	2.177	2.177	-
Methoxyphenol	0.009	0.009	0.009	-
Silicone compound (F-1)	0.136	0.136	0.136	-
SF-8421	-	-	-	0.408
Solsperse 20000	-	-	-	4.292
Total	100	100	100	100
Methyl ethyl ketone	83.714	83.714	83.714	-
Methyl isobutyl ketone	139.640		139.640	-
IPA	34.474	174.11	34.474	90.129
Toluene	-		-	24.464
Solid content (wt%)	27.9	27.9	27.9	-
Properties of cured film				
Surface resistivity (ohm/square)	10 ¹⁰	10 ¹¹	10 ¹²	10 ⁸
Scratch resistance	Good	Good	Good	Bad

Zinc antimonate particles (zinc antimonate double oxide, "Celnax CX-210IP" manufactured by Nissan Chemical Industries, Ltd.; dispersion medium: isopropanol, solid content: 20.9 wt%)

ATO (antimony-doped tin oxide particles, "SN-100P" manufactured by Ishihara Sangyo Kaisha, Ltd.)

Tris(2-hydroxyethyl)isocyanurate acrylate ("Aronix M-315" manufactured by Toagosei Co., Ltd.)

1-Hydroxycyclohexyl phenyl ketone (photoinitiator, "Irgacure 184" manufactured by Ciba Specialty Chemicals Inc.)

10 2-Methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one (photoinitiator, "Irgacure 907" manufactured by Ciba Specialty Chemicals Inc.)

Methoxyphenol (a polymerization inhibitor, manufactured by Wako Pure Chemical Industries, Ltd.)

15 Epoxy polyether-modified silicone oil ("SF-8421" manufactured by Dow Corning Toray Co., Ltd.)

Solsperse 20000 (manufactured by Zeneca)

As is clear from the results shown in Table 1, it was found that the composition of the example, which contains only a small amount of conductivity providing component (zinc antimonate particles), produces a cured film having a low surface resistivity and exhibiting excellent scratch resistance. It was found that the composition of Comparative Example 1, which contains ATO commonly used as the conductivity providing component in an amount equal to the amount of zinc antimonate particles used in Examples 1 and 2, produces a cured film having a higher surface resistivity in comparison with Examples 1 and 2. Therefore, it is necessary to use a large amount of ATO in order to achieve a sufficiently low surface resistivity. It was also found that the composition of Comparative Example 2 (equivalent to the resin composition disclosed in the patent document 1) produces a cured film having a low surface resistivity but exhibiting poor scratch resistance.

The curable composition of the present invention and the cured product of the curable composition are useful for an application which requires antistatic properties and scratch resistance, particularly as a hard coating for a printer belt or printer drum.

Brief Description of the Drawings

35 FIG. 1 shows a conceptual diagram of a structure of a laser printer using an intermediate transfer belt method.

FIG. 2 shows a conceptual diagram of a structure of a laser printer using a transfer drum method.

FIG. 3 shows a conceptual diagram of a structure of a laser printer using a tandem method.

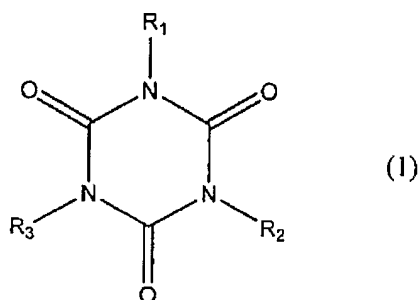
5 FIG. 4 shows a conceptual diagram of a structure of an ink-jet printer.

Explanation of Symbols

- | | |
|----|------------------------------------|
| | 1. transfer (resin) belt |
| | 2. transfer paper |
| 10 | 3. toner |
| | 4. development unit |
| | 5. photo-writing unit |
| | 6. electrostatic charger |
| | 7. photosensitive drum |
| 15 | 8. fixing unit |
| | 9. driving roller |
| | 10. driven roller |
| | 11. transfer chager |
| | 21. adhesion transfer (resin) belt |
| 20 | 22, 22a. recording paper |
| | 23. feeding unit |
| | 24. feeding roller |
| | 25. transfer roller |
| | 26. driven roller |
| 25 | 27. pressure roller |
| | 28. pinch roller |
| | 29. driving roller |
| | 30. platen unit |
| | 31. electrostatic brush |
| 30 | 32. recording head |
| | 33. spur |
| | 34. unloading roller |
| | 35. receiving tray |
| | 36. transfer drum |
| 35 | 37. laser exposure unit |
| | 38. rotary development unit |

CLAIMS

- 1 A curable composition, comprising: (A) 5 to 50 wt% of zinc antimonate
 5 particles; and (B) 10 to 50 wt% of a compound shown by the following formula
 (1),



- 10 wherein R^1 , R^2 , and R^3 individually represent monovalent organic groups, with
 at least two of R^1 , R^2 , and R^3 being $-R^4OCOCR^5=CH_2$, R^4 represents a
 divalent organic group having 2 to 8 carbon atoms, and R^5 represents a
 hydrogen atom or a methyl group; the amount of each component being
 based on the total amount of the composition excluding a solvent.
- 15 2. The curable composition according to claim 1, wherein the component (B) is
 tris((meth)acryloxyethyl) isocyanurate.
3. The curable composition according to claim 1 or 2, further comprising (C) 10
 to 70 wt% of a polyfunctional (meth)acrylate compound other than the
 components (A) and (B), based on the total amount of the composition
 excluding a solvent.
- 20 4. The curable composition according to any of claims 1 to 3, wherein the
 composition containing the component (B) in an amount of 20 wt% or more for
 100 wt% of the total (meth)acrylate component in the composition excluding
 the component (A).
- 25 5. A cured film produced by curing the curable composition according to any of
 claims 1 to 4.
6. The cured film according to claim 5, the cured film being a hard coating film for
 a printer belt.
7. The cured film according to claim 5, the cured film being a hard coating film for
 a printer drum.
- 30 8. A laminate comprising the cured film according to claim 5.

Figure 1/4

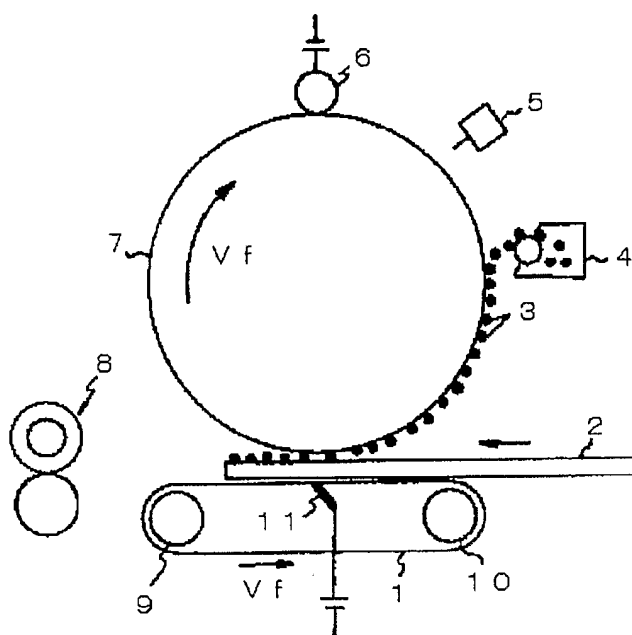


Figure 2/4

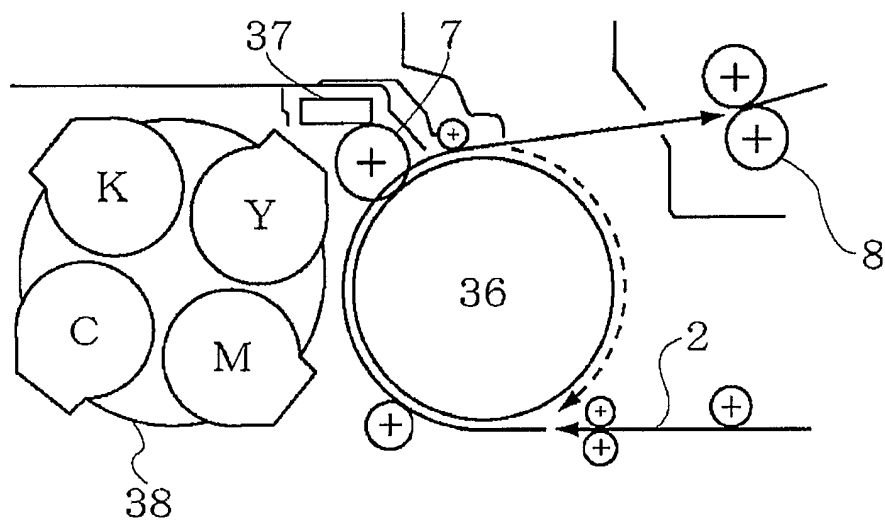


Figure 3/4

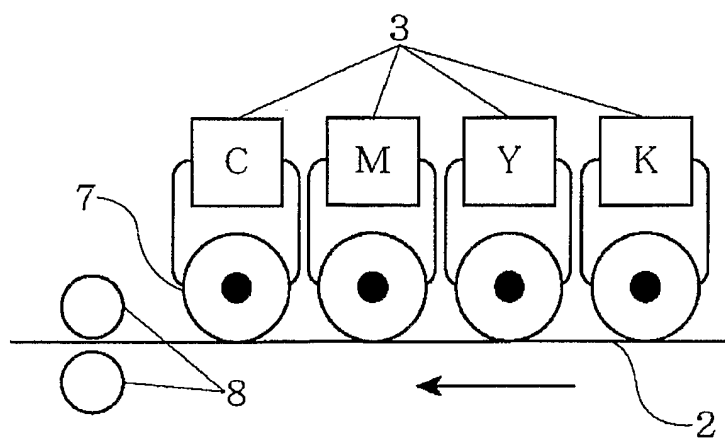
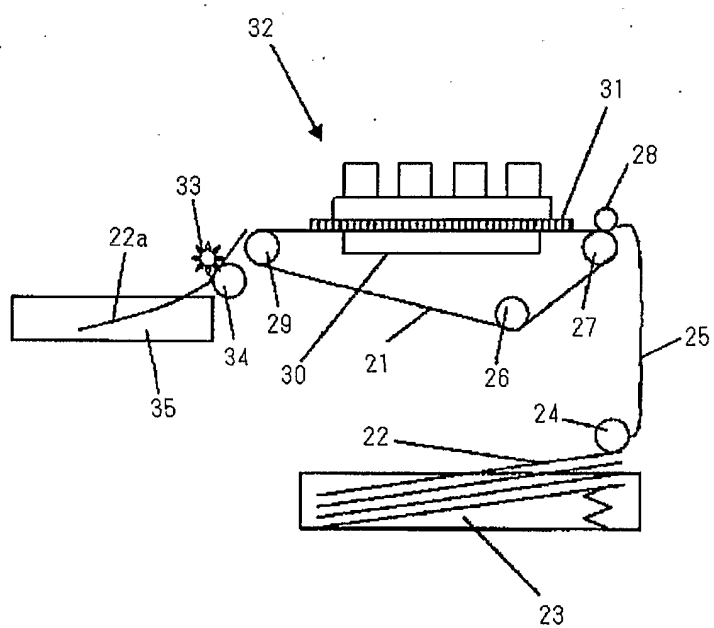


Figure 4/4



INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2005/000870

A. CLASSIFICATION OF SUBJECT MATTER

C09D4/00

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

B. FIELDS SEARCHED

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

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

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

EPO-Internal, PAJ, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 08, 6 October 2000 (2000-10-06) & JP 2000 127288 A (MITSUBISHI GAS CHEM CO INC), 9 May 2000 (2000-05-09) abstract	1-8
X	PATENT ABSTRACTS OF JAPAN vol. 2003, no. 12, 5 December 2003 (2003-12-05) & JP 2004 122611 A (TOPPAN PRINTING CO LTD), 22 April 2004 (2004-04-22) abstract	1-8
	----- -/-	

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

☒ See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

23 March 2006

Date of mailing of the international search report

29/03/2006

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INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2005/000870

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 10, 31 October 1997 (1997-10-31) & JP 09 169952 A (NIKON CORP; NASU NIKON:KK), 30 June 1997 (1997-06-30) abstract	1-8
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 14, 31 December 1998 (1998-12-31) & JP 10 231444 A (NIPPON KAYAKU CO LTD), 2 September 1998 (1998-09-02) cited in the application abstract	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/NL2005/000870

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JP 2004122611	A	22-04-2004	NONE	
JP 09169952	A	30-06-1997	NONE	
JP 10231444	A	02-09-1998	NONE	