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(54) **Title:** LIGHT-SHIELDING COMPOSITION, METHOD FOR PRODUCING A LIGHT-SHIELDING COMPOSITION, SOLDER RESIST, METHOD FOR FORMING A PATTERN, AND SOLID-STATE IMAGING DEVICE

(57) **Abstract:** The invention provides a light-shielding composition which has suitability for thick film formation, provides a film having an excellent coating uniformity, has thickness uniformity on uneven surface, and has an excellent light-shielding property of light in an infrared region. The light-shielding composition includes: (A) any one of a light-shielding particle or a light-shielding dye; (B) a first filler having a particle diameter of from 100 nm to 3,000 nm, the particle diameter being a maximum value in a particle diameter distribution of the first filler; and (C) a second filler having a particle diameter of from 5 nm to 90 nm, the particle diameter being a maximum value in a particle diameter distribution of the second filler.



DESCRIPTION

LIGHT-SHIELDING COMPOSITION, METHOD FOR PRODUCING A LIGHT-SHIELDING COMPOSITION, SOLDER RESIST, METHOD FOR FORMING A PATTERN, AND SOLID-STATE IMAGING DEVICE

Technical Field

[0001] The present invention relates to a light-shielding composition, a method for producing a light-shielding composition, a solder resist formed using the light-shielding composition, a method for forming a pattern, and a solid-state imaging device.

Background Art

[0002] Solid-state imaging devices used for cellular phones, digital cameras, digital videos, security cameras and the like are photoelectric conversion devices which are integrated as circuits using production techniques of semiconductor devices. In accordance with the recent trend towards miniaturization and weight reduction of cellular phones and digital cameras, miniaturization of solid-state imaging devices has been further demanded.

In order to realize miniaturization of solid-state imaging devices, application of through electrodes and methods of formation of thin-film silicon wafers are suggested. Miniaturization of solid-state imaging devices can be realized by forming silicon wafers in thin films through a polishing process. However, while thin-film silicon wafers maintain light-shielding property with respect to light with a wavelength of 800 nm or less, light with a wavelength of 800 nm or higher tends to be easily transmitted therethrough. It was found that, since photodiodes used for solid-state imaging devices are capable of reacting even with light with a wavelength from 800 nm to 1200 nm, light with a wavelength of 800 nm or higher easily transmits, and thus a new problem of the deterioration of image quality is caused.

[0003] The configuration of a solid-state imaging device is as follows. That is, in a solid-state imaging device, a color filter and a lens are arranged adjacent to one side of a photodiode, and an infrared cut filter is present around the color filter or the lens and thus blocks light with a wavelength 800 to 1200 nm, while metal wirings, a solder resist, and the like are present at the opposite side of the color filter. The gaps between metal wirings and the like may be often embedded with a solder resist, but there is a problem in that infrared light such as leaked light which is incorporated in cellular phones, digital cameras and the like cannot be blocked. Accordingly, there has conventionally been a need for methods for securing an infrared light-shielding property by forming a light-shielding layer on a solder

resist that has poor light-shielding properties with respect to infrared light.

[0004] At present, an infrared light-shielding layer is separately formed after a solder resist has been formed by a coating method. For this reason, a series of processes including coating, light exposure, development and post-heating processes and the like are required in order to form the solder resist and the infrared light-shielding layer. This may make the overall process complicated and cause increase in costs. For this reason, the improvement for this was desired.

[0005] In an infrared light-shielding layer, carbon black (for example, see Japanese Patent Application Laid-Open (JP-A) No. 2009-276406), titanium black (for example, see JP-A No. 2002-285007), cesium tungsten oxide (for example, see JP-A No. 2009-205029) or the like may be used. However, when a filling layer is formed instead of a solder resist in the gaps between the metal wirings using any one of these techniques, sufficient filling is not achieved, the obtained filling layer has a nonuniform surface, and steps (i.e., unevenness) caused by metal wirings and the like cannot be eliminated. That is, formability of thick films is low, the surface properties of the obtained films are poor, and "thickness uniformity on uneven surface" is deteriorated.

[0006] In an attempt to solve these problems, methods for imparting an infrared light-shielding property to a solder resist are considered. For example, a black solder resist composition which contains a black colorant, a colorant other than the black colorant, and a multifunctional epoxy compound is suggested (for example, see JP-A No. 2008-257045). However, since this composition contains a reduced content of black colorant by using the black colorant in combination with a colorant other than the black colorant, light-shielding properties, in particular, light-shielding properties in an infrared range are insufficient, and "suitability for thick film formation" is insufficient, which make the composition practically inapplicable.

SUMMARY OF INVENTION

Technical Problem

[0007] In general, in order to avoid coating unevenness (e.g., film thickness unevenness, deterioration in surface property, and the like) of coated films in a spin coating method used for semiconductor processes, application at a number of revolutions of 900 rpm or higher is commonly required. However, the unevenness due to the metal wirings generally has a difference in height of about 20 μm , and therefore it is required to apply a coating film such as a solder resist layer having a thickness of about 24 μm or more by spin-coating (in the present invention, referred to as "suitability for thick film formation" which means the suitability of

the composition for forming a thick coated film), in order to planarize the unevenness. In addition, it is required that the obtained film has a uniform surface (in the present invention, referred to as "coating uniformity").

[0008] In addition, it is generally required that a solder resist after coating is cured by irradiation with a UV ray or the like. However, when a solder resist layer is formed on a substrate that has unevenness due to metal wirings and the like, the film thickness in a concave region between metal wirings increases, and, as a result, irradiation of UV light to the lowermost layer of solder resist layer is difficult, thus the solder resist layer causes problems such as insufficient curing of the lower layer or, in the most serious cases, "film peeling".

That is, it is necessary that the film that is present over the gaps between metal wirings has substantially the same thickness as that present over the metal wirings (in the present invention, referred to as "thickness uniformity on uneven surface").

In addition, it is required that the solder resist has a high-temperature and/or high-humidity resistance or is free of cracks.

[0009] The present invention is made to satisfy the above-mentioned requirements of a solder resist and the like, and to approach conventional problems.

That is, an object of the present invention is to provide a light-shielding composition that has suitability for thick film formation, is capable of imparting excellent coating uniformity to the obtained film, has thickness uniformity on uneven surface and exhibits a superior blocking property in the infrared light range. In addition, another object of the present invention is to provide a method for producing the light-shielding composition, a solder resist, a method for forming a pattern using the solder resist, and a high-resolution solid-state imaging device.

Solution to Problem

[0010] Aspects of the present invention are as follow.

<1> A light-shielding composition, including:

(A) any one of a light-shielding particle or a light-shielding dye;

(B) a first filler having a particle diameter of from 100 nm to 3,000 nm, the particle diameter being a maximum value in a particle diameter distribution of the first filler; and

(C) a second filler having a particle diameter of from 5 nm to 90 nm, the particle diameter being a maximum value in a particle diameter distribution of the second filler, wherein, when the (B) first filler and the (C) second filler are mixed in the light-shielding composition, the particle diameter distribution among the mixed fillers includes a maximum value within a range from 5 nm to 90 nm and a maximum value within a range from 100 nm

to 3,000 nm.

[0011] <2> The light-shielding composition according to <1>, wherein the light-shielding particle is a pigment.

<3> The light-shielding composition according to <1> or <2>, wherein the light-shielding particle is an inorganic pigment.

<4> The light-shielding composition according to any one of <1> to <3>, wherein the particle diameter of the light-shielding particle is from 5 nm to 100 nm, the particle diameter being a maximum value in a particle diameter distribution of the light-shielding particle.

[0012] <5> The light-shielding composition according to any one of <1> to <4>, wherein the light-shielding particle is at least one selected from the group consisting of titanium black, carbon black, and cesium tungsten oxide.

<6> The light-shielding composition according to any one of <1> to <5>, wherein at least one of the (B) first filler or the (C) second filler is an inorganic filler.

[0013] <7> The light-shielding composition according to any one of <1> to <6>, wherein at least one of the (B) first filler or the (C) second filler is silica.

<8> The light-shielding composition according to any one of <1> to <7>, wherein at least one of the (B) first filler or the (C) second filler has a substantially spherical shape.

<9> The light-shielding composition according to any one of <1> to <8>, wherein a ratio of contents of the (B) first filler and the (C) second filler is from 1:30 to 1:2 in mass basis.

[0014] <10> The light-shielding composition according to any one of <1> to <9>, further including:

(D) a polymerizable compound; and

(E) a photopolymerization initiator.

<11> A method of producing the light-shielding composition according to any one of <1> to <10>, including:

mixing a dispersion including the light-shielding particle, a dispersion including the (B) first filler, and a dispersion including the (C) second filler, which are prepared as separate dispersions.

[0015] <12> A solder resist, including the light-shielding composition according to any one of <1> to <10>.

<13> A method of producing a pattern, including:

forming a photosensitive layer using the solder resist according to <12> on a substrate;

subjecting the photosensitive layer to pattern light exposure to cure an exposed region thereof; and

subjecting the photosensitive layer after the pattern light exposure to alkali development.

<14> A solid-state imaging device, having at least a solder resist layer formed using the solder resist according to <12>.

[0016] The light-shielding composition according to an aspect of the present invention contains (A) one of a light-shielding particle and a light-shielding dye, (B) a first filler, and (C) a second filler, and has suitability for thick film formation, and the obtained film has excellent coating uniformity and superior thickness uniformity on uneven surface.

The reason for this may be considered to be as follows. Since the light-shielding composition of the present invention contains (B) a first filler having a relatively large particle diameter and (C) a second filler having a relatively small particle diameter, it is assumed that the (B) and (C) fillers in the light-shielding composition form a cross-linking-like structure, together with a dispersant and the like. By forming a cross-linking-like structure, when a high shear rate is applied during an application process, a thick coating layer is formed in substantially the same thickness over the metal wirings and over the gaps between metal wirings, and suitability for thick film formation is improved, even when unevenness due to metal wirings and the like is present.

Furthermore, during the drying process, a shear rate is decreased and the obtained coating layer (having substantially the same film thickness over the metal wirings and over the gaps between the metal wirings) does not cause flow during drying and maintains its thickness and thus exhibits good thickness uniformity on uneven surface. Also, even when the obtained coating layer is heated for curing and the like, flowability is restricted due to the cross-link-like structure, heat slack is thus prevented and good thickness uniformity on uneven surface is maintained.

Also, the obtained film has a uniform surface property, and excellent coating uniformity is exhibited. The reason for this is considered to be that (B) a first filler having a large particle diameter and (C) a second filler having a small particle diameter are densely filled, resulting in a superior surface property.

Advantageous Effects of Invention

[0017] According to an aspect of the invention, a light-shielding composition is provided, which has suitability for thick film formation, is capable of imparting an excellent coating uniformity to the obtained films, has thickness uniformity on uneven surface and exhibits a

superior light-shielding property in an infrared range. In addition, according to another aspect of the invention, there are provided a method for producing a light-shielding composition, a solder resist, a method for forming a pattern using the solder resist and a solid-state imaging device having a high resolution.

BRIEF DESCRIPTION OF DRAWINGS

[0018] Fig. 1 is a schematic view illustrating the configuration of a camera module including a solid-state imaging device according to an exemplary embodiment of the invention; and

Fig. 2 is a schematic cross-sectional view illustrating a solid-state imaging device according to an exemplary embodiment of the invention.

DESCRIPTION OF EMBODIMENTS

[0019] Hereinafter, a light-shielding composition, a method for producing a light-shielding composition, a solder resist using the light-shielding composition, and a solid-state imaging device according to the present invention will be described in detail.

In addition, in the present specification, a group (atomic group) in which its substitution or un-substitution is not disclosed may have no substituent or have one or more substituents. For example, the term "alkyl group" includes an alkyl group that has no substituent (i.e., unsubstituted alkyl group) and an alkyl group that has one or more substituents (i.e., a substituted alkyl group). In addition, in the present specification, the viscosity means a value measured at 25°C.

[0020] The light-shielding composition of the present invention contains at least: (A) any one of a light-shielding particle or a light-shielding dye, (B) a first filler having a particle diameter of from 100 nm to 3,000 nm, the particle diameter being a maximum value in a particle diameter distribution, and (C) a second filler having a particle diameter of from 5 nm to 90 nm, the particle diameter being a maximum value in a particle diameter distribution, and may optionally contain (D) a polymerizable compound, and (E) a photopolymerization initiator, an alkali-soluble binder, a dispersant, a sensitizing agent, a cross-linking agent, a hardening accelerator, an elastomer, a surfactant and other component.

[0021] The light-shielding composition of the present invention is preferably a negative-working composition. Hereinafter, components of the composition will be described.

The description of constituent components mentioned below may be based on exemplary embodiments of the present invention, but the present invention is not limited to these embodiments. In addition, in this specification, a value range which is represented by "to" or "from ... to ..." indicates a range including values mentioned before and after "to" as a

lower limit and an upper limit, respectively.

In addition, in the present specification, the term "(meth)acrylate" means acrylate and methacrylate, the term "(meth)acryl" means acryl and methacryl, and the term "(meth)acryloyl" means acryloyl and methacryloyl. In addition, in the present specification, the term "monomeric compound" is the same as term "monomer". In the present invention, the monomer means a compound having a weight average molecular weight of 2,000 or less, which is different from an oligomer and a polymer. In the present specification, the polymerizable compound refers to a compound having a polymerizable group and may be a monomer or a polymer. The polymerizable group refers to a group which mediates a polymerization reaction.

[0022] *(A) Light-shielding particle and light-shielding dye*

The light-shielding composition of the present invention contains (A) at least one of a light-shielding particle or a light-shielding dye.

Preferably, the light-shielding particle and light-shielding dye used for the present invention absorb light with a wavelength of from 800 nm to 1,200 nm and exhibit superior light-transmittance of light use for light exposure.

In addition, the light-shielding particle and light-shielding dye used for the present invention may be either a light-shielding dye or light-shielding particle which absorbs light with a wavelength of from 800 nm to 1,200 nm. A light-shielding particle is preferred in terms of heat resistance.

Examples of the dye that can be used as a light-shielding dye in the present invention include cyanine colorants, phthalocyanine colorants, naphthalocyanine colorants, immonium colorants, aminium colorants, quinolium colorants, pyrylium colorants, and metal complex colorants such as Ni complex colorants.

[0023] In addition, the light-shielding particle is preferably a pigment selected from organic pigments and inorganic pigments in terms of heat resistance, and is particularly preferably an inorganic pigment.

Examples of infrared light-absorbing inorganic pigment which may be used as the light-shielding particle in the present invention include carbon black, titanium black, tungsten compounds, zinc oxide, white lead, lithopone, titanium oxide, chromium oxide, iron oxide, precipitated barium sulfate and barite powders, red lead, red iron oxide, yellow lead, zinc chromate (zinc chromate type 1, zinc chromate type 2), ultramarine blue, Prussian blue (potassium ferricyanide), zircon gray, praseodymium yellow, chromium titanate yellow, chromium green, peacock, Victoria green, iron blue (un-related to Prussian blue), vanadium zirconium blue, chromium tin pink, manganese pink, and salmon pink. In addition,

examples of useful black pigments include metal oxides, metal nitrides or a mixture thereof which includes one or more metal elements selected from the group consisting of Co, Cr, Cu, Mn, Ru, Fe, Ni, Sn, Ti and Ag.

[0024] Among these inorganic pigments, carbon black, titanium black, and tungsten compounds are preferred in terms of an infrared light-shielding property, and titanium black and tungsten compounds are more preferred.

[0025] The titanium black in the present invention refers to black particles having titanium atoms. Low-oxidation number titanium oxide, titanium oxynitride or the like is preferred. Surface-modified particles may be used as the titanium black particles in order to improve dispersibility and suppresses aggregation.

For example, the surface-modification may be carried out by coating with one or more selected from silicon oxide, titanium oxide, germanium oxide, aluminum oxide, magnesium oxide and zirconium oxide. Alternatively, the surface may be treated with a water-repellent substance disclosed in the paragraphs [0010] to [0027] of Japanese Patent Application Laid-Open (JP-A) No. 2007-302836.

[0026] Examples of methods for producing titanium black include, but are not limited to, reduction of a mixture of titanium dioxide and titanium metal by heating under a reduction atmosphere (see, for example, JP-A No. 49-5432), reduction of ultrafine titanium dioxide obtained by high-temperature hydrolysis of titanium tetrachloride under a reduction atmosphere containing hydrogen (see, for example, JP-A No. 57-205322), reduction of titanium dioxide or titanium hydroxide in the presence of ammonia at a high-temperature (see, for example, JP-A No. 60-65069, or JP-A No. 61-201610), reduction of a vanadium compound linked to titanium dioxide or titanium hydroxide in the presence of ammonia at a high-temperature (see, for example, JP-A No. 61-201610) and the like.

[0027] In addition, the light-shielding particle used in the present invention is more preferably a tungsten compound from the viewpoint of low absorbance to visible light.

[0028] The tungsten compound is a light-shielding particle which has a high absorbance to infrared light (with a wavelength of about 800 nm to 1,200 nm) (that is, has a high light-shielding property (shielding property) with respect to infrared light) and a low absorbance to visible light. Accordingly, when the light-shielding composition of the present invention contains a tungsten compound, a pattern that exhibits a high light-shielding property in an infrared light and a high transmittance property in a visible light is formed.

In addition, the tungsten compound also exhibits a low absorbance to light that has a lower wavelength than visible light that is used for light exposure by high pressure mercury lamps, KrF, ArF and the like used for image formation. Accordingly, a superior pattern

formability may be obtained by using the tungsten compound in combination with a photopolymerization initiator, a polymerizable compound and the like.

[0029] Examples of the tungsten compound include tungsten oxide compounds, tungsten boride compounds, and tungsten sulfide compounds. The tungsten compound is more preferably a tungsten oxide compound represented by the following Formula (I).



In Formula (I), M represents a metal, W represents tungsten and O represents oxygen, and $0.001 \leq x/y \leq 1.1$, and $2.2 \leq z/y \leq 3.0$.

[0030] Examples of the metal represented by M in Formula (I) include alkali metals, alkaline earth metals, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Al, Ga, In, Tl, Sn, Pb, Ti, Nb, V, Mo, Ta, Re, Be, Hf, Os, and Bi. The metal represented by M may be one type of metals, or may include two or more types thereof.

[0031] M is preferably an alkali metal, more preferably Rb or Cs, and further more preferably Cs.

[0032] When x/y is 0.001 or more, infrared light is sufficiently shielded, and when x/y is 1.1 or less, formation of impurities in the tungsten compound is reliably prevented.

When z/y is 2.2 or more, chemical stability of the material is further improved, and when z/y is 3.0 or less, infrared light is sufficiently shielded.

[0033] Specific examples of the tungsten oxide compounds represented by Formula (I) include $Cs_{0.33}WO_3$, $Rb_{0.33}WO_3$, $K_{0.33}WO_3$, and $Ba_{0.33}WO_3$. Furthermore, $Cs_{0.33}WO_3$ or $Rb_{0.33}WO_3$ is preferred, and $Cs_{0.33}WO_3$ (cesium tungsten oxide) is more preferred from the viewpoint of visibility in visible light.

[0034] The tungsten compound is commercially available. When the tungsten compound is, for example, a tungsten oxide compound, the tungsten oxide compound may be obtained by heating a tungsten compound under an inert gas atmosphere or a reducing gas atmosphere (see, for example, Japanese Patent No. 4096205).

In addition, the tungsten oxide compound may be, for example, available as a dispersion of tungsten particles such as YMF-02 (trade name, manufactured by Sumitomo Metal Mining Co., Ltd.).

[0035] The light-shielding particle is preferably a fine particle, and preferably has a particle diameter the indicates a maximum value in a particle diameter distribution thereof, of 5 nm to 100 nm, more preferably 5 to 50 nm, and most preferably 5 nm to 30 nm.

When the particle diameter is within the above ranges, precipitation of light-shielding particles over time decreases, and stability of light-shielding composition of the present invention over time is further improved.

[0036] The particle diameter of the light-shielding particle, and the particle diameter distributions of the (B) and (C) fillers mentioned below may be measured in the following manner: that is, a dispersion containing light-shielding particles or a dispersion containing (B) and (C) fillers, which is the target of particle diameter distribution measurement, is diluted with propylene glycol monomethyl ether acetate (x100); the dilution is dropped on a carbon foil, followed by drying; and the dried dilution is observed using a transmission electron microscope (TEM) to measure the particle diameters. Evaluation of the particle diameter is carried out by evaluating particle diameters based on a circular shape, drawing a particle diameter distribution graph with the number of samples being 400, a particle diameter is plotted at a horizontal axis, appearance frequency is plotted at a longitudinal axis and a particle diameter having a maximum value is present on the graph, and evaluating the particle diameter as "a particle diameter that exhibits a maximum value in a particle diameter distribution".

In addition, unless specifically otherwise noted in the present specification, the term "particle diameter" refers to a volume average particle diameter.

[0037] Two or more types of light-shielding particle and light-shielding dye may be used in the light-shielding composition of the present invention. In this case, two or more types of the light-shielding particles may be used, or two or more types of the light-shielding dyes may be used, or a combination of one or more types of the light-shielding particles and one or more types of the light-shielding dyes may be used. In any case, different types or the same type of the light-shielding particles and the light-shielding dye may be used, respectively.

The content (i.e., total content) of the (A) light-shielding particle and/or light-shielding dye is preferably in a range of from 3% by mass to 30% by mass, and more preferably from 5% by mass to 20% by mass, with respect to the total solid mass of the light-shielding composition of the present invention.

The total solid mass of the light-shielding composition in the present invention refers to the total content (mass) of the components of the composition except a solvent.

[0038] *(B) First filler and (C) second filler*

The light-shielding composition of the present invention contains (B) a first filler having a particle diameter that is a maximum value in a particle diameter distribution of in a range of from 100 nm to 3,000 nm (hereinafter, referred to as "(B) filler" or "first filler"), and (C) a second filler having a particle diameter that is a maximum value in a particle diameter distribution of in a range of from 5 nm to 90 nm (hereinafter, referred to as "(C) filler" or "second filler").

Hereinafter, the (B) filler and (C) filler will be described.

[0039] The (B) filler and (C) filler may each be an organic filler, an inorganic filler, an inorganic-organic compound filler or the like, or alternatively, a combination of two or more thereof may be used. Preferably, at least one of (B) filler or (C) filler is an inorganic filler.

[0040] Examples of the organic filler include synthetic resin particles and natural polymer particles. Preferred examples thereof include resin particles of an acrylic resin, polyethylene, polypropylene, polyethylene oxide, polypropylene oxide, polyethylene imine, polystyrene, polyurethane, polyurea, polyester, polyamide, polyimide, and the like, and carboxymethyl cellulose, gelatin, starch, chitin, and chitosan. More preferred are resin particles of an acrylic resin, polyethylene, polypropylene, polystyrene, and the like.

Specific examples of commercially available fillers preferable as the organic filler include CHEMIPEARL W100, W200, W300, W308, W310, W400, W401, W4005, W410, W500, WF640, W700, W800, W900, W950, WP100 (trade names, manufactured by Mitsui Chemicals, Inc.), MX-150, MX-180, MX-300, MX-500, MX-1000, MX-1500 H, MX-2000, MR-2HG, MR-7HG, MR-10HG, MR-3GSN, MR-5GSN, MR-2G, MR-7G, MR-10G, MR-20G, MR-5C, MR-7GC, SX-130H, SX-350H, SX-500H, SGP-50C, SGP-70C (trade names, manufactured by Soken Chemical & Engineering Co., Ltd.), and MBX-5, MBX-8, MBX-12, MBX-15, MBX-20, MB20X-5, MB30X-5, MB30X-8, MB30X-20, SBX-6, SBX-8, SBX-12, SBX-17 (trade names, manufactured by Sekisui Plastics Co., Ltd) and the like.

[0041] Examples of the inorganic fillers include metals and metal compounds such as oxides, composite oxides, hydroxides, carbonates, sulfates, silicates, phosphates, nitrides, carbides and sulfides and combinations of at least two kinds thereof. Specific examples include silica, mica compounds, glass, zinc oxide, alumina, zirconium oxide, stannic oxide, potassium titanate, strontium titanate, aluminum borate, magnesium oxide, magnesium borate, aluminum hydroxide, magnesium hydroxide, calcium hydroxide, titanium hydroxide, basic magnesium sulfate, calcium carbonate, magnesium carbonate, calcium sulfate, magnesium sulfate, calcium silicate, magnesium silicate, calcium phosphate, silicon nitride, titanium nitride, aluminum nitride, silicon carbide, titanium carbide, zinc sulfide and compounds of at least two kinds thereof.

Preferred are silica, mica compounds, glass, alumina, potassium titanate, strontium titanate, aluminum borate, magnesium oxide, calcium carbonate, magnesium carbonate, calcium silicate, magnesium silicate, calcium phosphate, calcium sulfate and the like.

[0042] Among the inorganic fillers, silica is preferred.

At least one of the (B) filler or (C) filler is preferably silica, and it is more preferable that both of the (B) filler and (C) filler are silica.

[0043] Examples of the form of the filler include a fiber shape, a needle shape, a planar

shape, a sphere shape, a tertrapod shape, a balloon shape and the like. Of these, a sphere shape is preferred.

At least one of the (B) filler or (C) filler has preferably a sphere shape, and it is more preferable that both of the (B) filler and (C) filler have a sphere shape.

[0044] The particle diameter of the (B) filler that indicates a maximum value in a particle diameter distribution of the (B) filler is 100 nm to 3,000 nm. When the particle diameter exceeds the upper limit of the range, coating uniformity of the light-shielding composition is deteriorated. When the particle diameter is lower than the lower limit of the range, moisture resistance of the light-shielding composition decreases.

The particle diameter of the (B) filler is preferably 100 nm to 1,600 nm, more preferably 100 nm to 900 nm, further more preferably 100 nm to 500 nm, still further more preferably 100 nm to 300 nm, and most preferably 200 nm to 300 nm.

When the particle diameter is within the above ranges, coating uniformity of a light-shielding composition is further improved.

[0045] The particle diameter of the (C) filler that indicates a maximum value in a particle diameter distribution of the (C) filler is 5 nm to 90 nm. When the particle diameter exceeds the upper limit of the range, the effect of the present invention upon thickness uniformity on uneven surface is almost completely not exhibited. In addition, when the particle diameter is lower than the lower limit of the range, the viscosity of dispersion is excessively increased and production efficiency is considerably deteriorated, when a dispersion of filler is prepared.

The particle diameter of the (C) filler is preferably 5 nm to 70 nm, more preferably 5 nm to 50 nm, even more preferably 5 nm to 40 nm, and most preferably 5 nm to 35 nm.

When the particle diameter is within the above ranges, thickness uniformity on uneven surface of light-shielding composition is further improved.

[0046] The light-shielding particles, and the (B) filler and (C) filler (hereinafter, all of light-shielding particles, (B) filler, and (C) filler may be collectively referred to as "respective particles") are preferably particles surface-treated with a silane coupling agent or the like mentioned below. By using the surface-treated particles, thermal cycle test resistance (TCT) and storage stability of a light-shielding composition are improved, for example, even after strict tests such as thermal cycle tests, the same good shape as in immediately after pattern formation can be further readily maintained.

[0047] *Silane coupling agent*

The silane coupling agent which is used for surface-treatment of particles is not particularly limited and may be suitably selected depending on the purpose. The silane coupling agent preferably has at least one functional group selected from an alkoxysilyl group,

a chlorosilyl group and an acetoxysilyl group (hereinafter, referred to as "first functional group") and at least one functional group selected from a (meth)acryloyl group, an amino group and an epoxy group (hereinafter, referred to as "second functional group"). The second functional group is more preferably a (meth)acryloyl group or an amino group, the second functional group is even more preferably a (meth)acryloyl group. When the second functional group is a (meth)acryloyl group, it is advantageous in terms of storage stability or TCT resistance.

[0048] In addition, a silane coupling agent as disclosed in JP-A No. 7-68256 may be preferably used, which has at least one functional group selected from an alkoxysilyl group, a chlorosilyl group and an acetoxysilyl group, as a first functional group, and at least one selected from an imidazole group, an alkylimidazole group and a vinylimidazole group, as a second functional group.

[0049] The silane coupling agent is not particularly limited, but examples of the preferable silane coupling agent include γ -aminopropyltriethoxysilane, N-(β -aminoethyl)- γ -aminopropyltrimethoxysilane, N-(β -aminoethyl)- γ -aminopropylmethyldimethoxysilane, γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropylmethyldimethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropylmethyldimethoxysilane, α -[[3-(trimethoxysilyl)propoxy]methyl]-imidazole-1-ethanol, 2-ethyl-4-methyl- α -[[3-(trimethoxysilyl)propoxy]methyl]-imidazole-1-ethanol, 4-vinyl- α -[[3-(trimethoxysilyl)propoxy]methyl]-imidazole-1-ethanol, 2-ethyl-4-methylimidazopropyltrimethoxysilane, which are disclosed in JP-A No. 7-68256, and salts, intramolecular condensates and intermolecular condensates thereof. These may be used alone or in combination of two or more types thereof.

[0050] The surface-treatment of particles with the silane coupling agent may be preliminarily applied to only each of the respective particles (in this case, hereinafter, may be referred to as "pre-treatment"), or may be applied to each of the respective particles together with a part or all of the other fillers to be contained in the light-shielding composition.

The pre-treatment is not particularly limited, but examples thereof include a dry-type method, an aqueous solution method, an organic solvent method, and a spray method. The pre-treatment temperature is not particularly limited, but is preferably room temperature to 200°C.

The pre-treatment is preferably performed together with addition of a catalyst. The catalyst is not particularly limited, and examples thereof include acids, bases, metal compounds, and organic metal compounds.

[0051] The amount of silane coupling agent to be added in a pre-treatment is not particularly

limited, but is preferably from 0.01 parts by mass to 50 parts by mass, and more preferably 0.05 parts by mass to 50 parts by mass, with respect to 100 parts by mass of each of the respective particles. When the amount of silane coupling agent to be added is within the above ranges, surface-treatment which is enough to obtain the desired effects is performed, and deterioration in handling caused by aggregation of respective particles after the surface-treatment is inhibited.

[0052] Since the first functional group in the silane coupling agent reacts with a surface of the base material, surfaces of the respective particles, and the active group of a binder, and the second functional group in the silane coupling agent reacts with the carboxyl group and ethylenically unsaturated group of the binder, adhesivity between a base material and a light-shielding composition layer is improved. Meanwhile, since the silane coupling agent has a high reactivity, the second functional group reacts or is deactivated due to diffusion during storage, when the silane coupling agent is incorporated into the light-shielding composition, and shelf life or pot life may be thus shortened.

[0053] However, as mentioned above, when the respective particles which have been pretreated with a silane coupling agent are used, diffusion action is inhibited and the problem of shelf life or pot life is considerably reduced, and use of an one-component solution is possible. When a sphere-shaped silica is subjected to a pre-treatment, stirring conditions, temperature conditions and catalyst use conditions may be freely selected. Therefore, reactivity between the first functional group in the silane coupling agent and the active group in the sphere-shaped silica may be thus considerably improved, as compared to a case in which addition is performed without a pre-treatment. Accordingly, in particular, considerably good results are obtained under strict requirements such as electroless gold plating, electroless solder plating and water-resistant load tests. Furthermore, the amount of silane coupling agent used may be reduced and shelf life and pot life may be further improved by performing a pre-treatment. Examples of sphere-shaped silica surface-treated with the silane coupling agent useful for the present invention include FB series and SFP series (trade names, manufactured by Denki Kogyo Co., Ltd.), 1-FX (trade name, manufactured by Tatsumori, Co., Ltd.), HSP series (trade name, manufactured by Toagosei Co., Ltd.), and SP series (trade name, manufactured by Fuso Chemical Co., Ltd.).

[0054] When the (B) first filler and the (C) second filler are mixed in the light-shielding composition of the invention, the particle diameter distribution among the mixed fillers (i.e., the (B) first filler and the (C) second filler) shows a bimodal particle diameter distribution with a maximum value in a range of from 5 nm to 90 nm and another maximum value in a range of 100 nm to 3,000 nm. The technical meanings of the lower and upper limits of the

above ranges are the same of those described for the (B) first filler and the (C) second filler.

[0055] In the light-shielding composition of the present invention, a ratio of a (B) filler content and a (C) filler content (i.e., (B) filler : (C) filler) is preferably from 1:30 to 1:2 in weight basis, and more preferably from 1:15 to 1:5 in weight basis. When the ratio is within the above ranges, thickness uniformity on uneven surface is improved.

[0056] The sum of a (B) filler content and a (C) filler content is preferably from 3% by mass to 30% by mass, more preferably from 5% by mass to 20% by mass, and more preferably from 6% by mass to 15% by mass, with respect to the total solid content of the light-shielding composition. When the sum is within the above ranges, transmittance in a visible light range is further improved.

Each of the (B) filler and (C) filler may be provided in one or more types, or one of them may be two or more types, or both of them may be two or more types.

[0057] *Preparation of particle dispersion*

As mentioned above, the light-shielding particles, (B) filler and (C) filler have been described. It is preferable to produce a dispersion of the light-shielding particles, a dispersion of the (B) filler and a dispersion of the (C) filler before the light-shielding composition is produced, by dispersing each of the respective particles together with a dispersant, an organic solvent and the like, which will be described later, through mixing and dispersing treatments while grinding the particles using a grinder such as bead mill or roll mill. By preparing respective dispersions, prior to preparation of the light-shielding composition, the respective particles may be dispersed into fine particles, and effects of the present invention are further attained.

The light-shielding dye may be not provided as a dispersion, and may be prepared as a light-shielding composition by dissolving it in an organic solvent or without any treatment. The light-shielding particles are preferably preliminarily prepared as a dispersion. Hereinafter, a case in which the light-shielding particles are used will be described, as one example.

Hereinafter, a dispersion of the light-shielding particle, a dispersion of the (B) filler, and a dispersion of the (C) filler may be collectively referred to as "particle dispersion", and preparation of such a particle dispersion will be described.

[0058] *Preparation of particle dispersion*

In a preferred embodiment of producing a light-shielding composition of the present invention, a light-shielding particle-containing dispersion, a dispersion containing a (B) first filler and a dispersion containing a (C) second filler are prepared by separately dispersing the light-shielding particles, the (B) first filler and the (C) second filler.

Each of the particle dispersions is obtained by dispersing any one of the light-shielding particles, (B) first filler, or (C) second filler in an organic solvent. At this time, a dispersant, a resin or the like may be optionally added. In addition, other components such as a pigment derivative may be optionally added.

As mentioned above, in accordance with a preferred embodiment, a light-shielding particle-containing dispersion, a dispersion containing a (B) first filler and a dispersion containing a (C) second filler are prepared by separately dispersing the light-shielding particles, the (B) first filler and the (C) second filler. Alternatively, a (B) first filler and a (C) second filler may be prepared in one dispersion, or the light-shielding particles, (B) first filler and (C) second filler may be prepared in one dispersion. Among these embodiments, to improve the freedom of treatment design (for example, variation in solid content or variation in viscosity to improve stability over time), it is preferable that a dispersion containing a (B) first filler and a dispersion containing a (C) second filler are prepared separately.

[0059] The preparation of particle dispersion is not particularly limited. For example, the particle dispersion may be obtained by subjecting any one of a light-shielding particle, a (B) first filler and a (C) second filler, or a dispersant and an organic solvent to a fine dispersion treatment using a vertical or horizontal-type sand grinder, a pin mill, a slit mill, an ultrasonic distributor or the like with beads which is made of glass, zirconium oxide, or the like and has a particle diameter of 0.01mm to 1mm.

[0060] Prior to the beads dispersion, a kneading dispersion treatment may be performed with applying a strong shear force using a two roll mill, a three roll mill, a ball mill, a trommel, a disperser, a kneader, a co-kneader, a homogenizer, a blender, a single-screw or twin-screw extruder or the like.

[0061] Details of kneading and dispersion are disclosed in, for example, T. C. Patton, "Paint Flow and Pigment Dispersion" (1964, published by John Wiley and Sons, Corp.).

[0062] *Dispersant*

The dispersant which is preferably contained in each of the particle dispersions will be described. When the particle dispersions each contain a dispersant, dispersibility and dispersion stability are improved.

[0063] Examples of the dispersant which may be used in the particle dispersion in the present invention include polymeric dispersants such as polyamide amines and salts thereof, polycarboxylic acids and salts thereof, high-molecular-weight unsaturated acid esters, modified polyurethanes, modified polyesters, modified poly(meth)acrylates, (meth)acrylic copolymers, or naphthalenesulfonate formalin condensates; and surfactants such as polyoxyethylene alkyl phosphates, polyoxyethylene alkylamines or alkanolamines.

The polymer dispersant may be classified into straight chain polymers, terminal-modified polymers, graft polymers, and block polymers, based on the structure thereof.

[0064] Examples of terminal-modified polymers having an anchor moiety for a surface include polymers having a terminal phosphate group, as disclosed in JP-A No. 3-112992, JP-A No. 2003-533455, and the like; polymers having a terminal sulfonate group, as disclosed in JP-A No. 2002-273191 or the like; polymers having a partial skeleton or heterocycle of organic pigment, as disclosed in JP-A No. 9-77994 or the like; and polymers prepared by modification of an oligomer or polymer having a hydroxyl group or amino group at one end thereof with an acid anhydride, as disclosed in JP-A No. 2008-29901 or the like. In addition, polymers in which at least two anchor moieties (such as an acidic group, a basic group, a partial skeleton or heterocycle of an organic pigment) for a surface of an infrared light-shielding material are introduced to an end of the polymers, as disclosed in JP-A No. 2007-277514 are also preferred because they exhibit a superior dispersion stability.

[0065] Examples of graft polymers having an anchor moiety for a surface include reaction products of a poly(lower alkylene imine) and a polyester as disclosed in JP-A No. 54-37082, Japanese National Phase Publication No. 8-507960, JP-A No. 2009-258668, or the like; reaction products of a polyarylamine and a polyester as disclosed in JP-A No. 9-169821 or the like; amphoteric dispersing resins having a basic group and an acidic group as disclosed in JP-A No. 2009-203462; copolymers of macromonomers and nitrogen atom-containing monomers as disclosed in JP-A No. 10-339949, JP-A No. 2004-37986 or the like; graft polymers having a partial skeleton or heterocycle of organic pigment as disclosed in JP-A No. 2003-238837, JP-A No. 2008-9426, JP-A No. 2008-81732 or the like; and copolymers of macromonomers and acidic group-containing monomers as disclosed in JP-A No. 2010-106268 or the like.

[0066] The macromonomers used for preparing the graft polymers having an anchor moiety for a surface by radical polymerization may be selected from known macromonomers. Examples thereof include macromonomers AA-6 (poly(methyl methacrylate) having a methacryloyl group as an end group), AS-6 (polystyrene having a methacryloyl group as an end group), AN-6S (a copolymer of styrene and acrylonitrile having a methacryloyl group as an end group), AB-6 (poly(butyl acrylate) having a methacryloyl group as an end group) (all trade names, manufactured by Toagosei Co., Ltd.); PLACCEL FM5 (an addition product of 2-hydroxyethyl methacrylate and 5 molar equivalents of ϵ -caprolactone), FA10L (an addition product of 2-hydroxyethyl acrylate and 10 molar equivalents of ϵ -caprolactone) (all trade names, manufactured by Daicel Chemical Industries Ltd.); and polyester macromonomers as disclosed in JP-A No. 2-272009 and the like. Among these monomers, in particular, polyester macromonomers which exhibit an excellent flexibility and an excellent solvent-

affinity are particularly preferably used in the light-shielding composition from the viewpoint of dispersibility and dispersion stability of an infrared light-shielding material and developability of the light-shielding compositions using the infrared light-shielding material, and polyester macromonomers typified by polyester macromonomers disclosed in JP-A No. 2-272009 are most preferred.

[0067] The block polymer having an anchor moiety for a surface is most preferably a block polymer as disclosed in JP-A No. 2003-49110, JP-A No. 2009-52010 and the like.

[0068] The dispersant may be, for example, suitably selected from known dispersants or surfactants.

Specific examples thereof include DISPERBYK-101 (polyamideamine phosphate), DISPERBYK-107 (carbonic acid ester), DISPERBYK-110 (a copolymer containing an acidic group), DISPERBYK-130 (polyamide), DISPERBYK-161, DISPERBYK-162, DISPERBYK-163, DISPERBYK-164, DISPERBYK-165, DISPERBYK-166, DISPERBYK-170 (high-molecular-weight copolymers) (all trade names, manufactured by BYK Japan K.K.); BYK-P104 and P105 (high-molecular-weight unsaturated polycarboxylic acid) (all trade names, manufactured by BYK Japan KK); EFKA 4047, 4050 to 4010 to 4165 (polyurethanes), EFKA 4330 to 4340 (block copolymers), EFKA 4400 to 4402 (modified-polyacrylates), EFKA 5010 (polyesteramide), EFKA 5765 (high-molecular-weight polycarboxylic acid salt), EFKA 6220 (fatty acid polyester), EFKA 6745 (phthalocyanine derivatives) (all trade names, manufactured by EFKA Chemicals Co., Ltd.); AJISPER PB821, PB822, PB880, PB881 (all trade names, manufactured by Ajinomoto Fine Techno Co., Inc.); FLUOREN TG-710 (urethane oligomer), POLYFLOW NO. 50 E, NO. 300 (acrylic copolymers) (all trade names, manufactured by Kyoeisha Chemical Co., Ltd.), DISPARLON KS-860, 873 SN, 874, # 2150 (aliphatic polyvalent carboxylic acids), # 7004 (polyether ester), DA-703-50, DA-705, DA-725 (all trade names, manufactured by Kusumoto Chemicals, Co., Ltd.); DEMOL RN, N (polycondensates of naphthalenesulfonic acid with formalin), MS, C, SN-B (polycondensates of aromatic sulfonic acid with formalin), HOMOGENOL L-18 (polycarboxylic acid polymer), EMULGEN 920, 930, 935, 985 (polyoxyethylene nonylphenyl ethers), ACETAMIN 86 (stearylamine acetate) (all trade names, manufactured by Kao Corporation); SOLSPERSE 5000 (phthalocyanine derivative), 13240 (polyesteramine), 3000, 17000, 27000 (polymers having a functional moiety at an end), 24000, 28000, 32000, 38500 (graft polymers) (all trade names, manufactured by The Lubrizol Corporation); NIKKOL T106 (polyoxyethylene sorbitan monooleate), MYS-IEX (polyoxyethylene monostearate) (all trade names, manufactured by Nikko Chemicals, Co., Ltd.); HINOACT T-8000 E and the like (trade name, manufactured by Kawaken Fine

Chemicals Co., Ltd.); organosiloxane polymer KP341 (trade name, manufactured by Shin-Etsu Chemical Co., Ltd.); W001 (cationic surfactant) (trade name, manufactured by Yusho Co., Ltd.); nonionic surfactants such as polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene nonylphenyl ether, polyethylene glycol dilaurate, polyethylene glycol distearate, or sorbitan fatty acid ester; anionic surfactants such as W004, W005, or W017; polymer dispersants such as EFKA-46, EFKA-47, EFKA-47EA, EFKA POLYMER 100, EFKA POLYMER 400, EFKA POLYMER 401, EFKA POLYMER 450 (all trade names, manufactured by Morishita & Co., Ltd); DISPERSE AID 6, DISPERSE AID 8, DISPERSE AID 15, DISPERSE AID 9100 (all trade names, manufactured by San Nopco Limited); ADEKA PLURONIC L31, F38, L42, L44, L61, L64, F68, L72, P95, F77, P84, F87, P94, L101, P103, F108, L121, P-123 (all trade names, manufactured by ADEKA Corporation); and IONET S-20 (trade name, manufactured by Sanyo Chemical Industries).

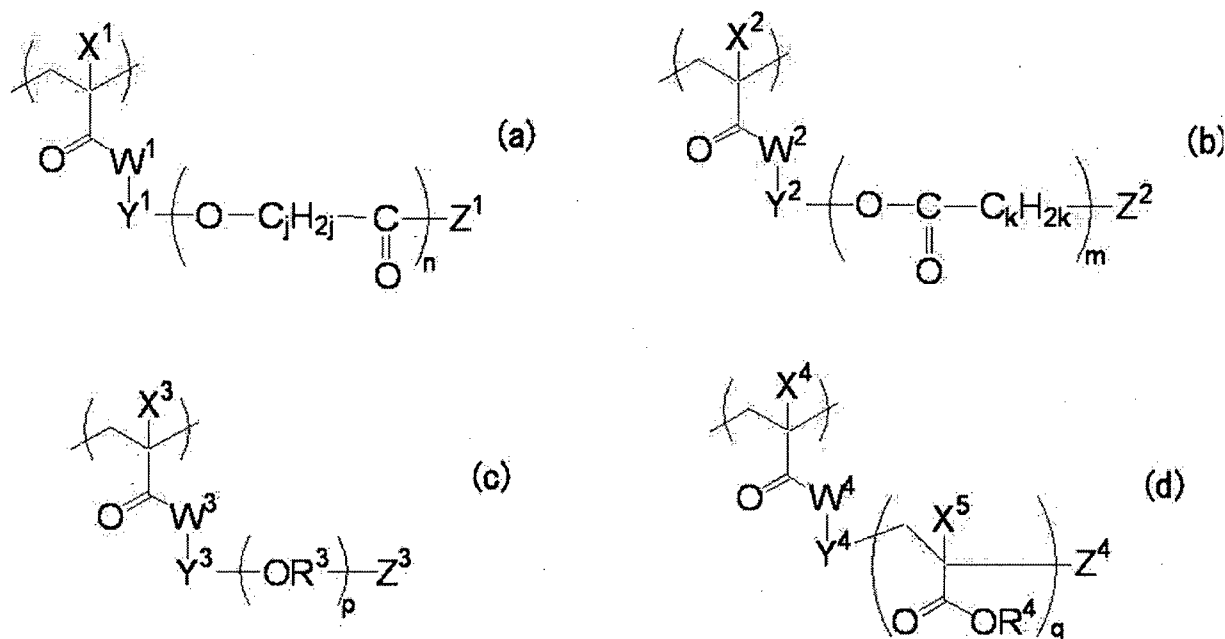
[0069] The dispersants may be used alone or in combination of two or more types thereof. The dispersant of the present invention may be used in combination with an alkali-soluble resin, together with the terminal-modified polymer, graft polymer, or block polymer having an anchor moiety for the surface of the light-shielding particle, (B) filler or (C) filler. Examples of the alkali-soluble resin include (meth)acrylic acid copolymers, itaconic acid copolymers, crotonic acid copolymers, maleic acid copolymers, partially-esterified maleic acid copolymers, acidic cellulose derivatives having a carboxylic acid group at a side chain thereof, and resins in which a polymer having a hydroxyl group is modified with an acidic anhydride. Particularly, (meth)acrylic acid copolymers are preferred. In addition, N position-substituted maleimide monomer copolymers as disclosed in JP-A No. 10-300922, ether dimer copolymers as disclosed in JP-A No. 2004-300204, and alkali-soluble resins having a polymerizable group as disclosed in JP-A No. 7-319161 are also preferred.

From the viewpoints of dispersibility, developability, and a precipitation property, the following resins as disclosed in JP-A No. 2010-106268 are particularly preferred. From the viewpoint of dispersibility, a polymer dispersant having a polyester chain at a side chain thereof is preferred. From the viewpoints of dispersibility and resolution of the patterns formed by a photolithographic method, a resin having an acidic group and a polyester chain is preferred. Preferable acidic groups that may be contained in the dispersant are preferably acidic groups having a pKa of 6 or less from the viewpoint of absorbability, and in particular, carboxylic acid, sulfonic acid and phosphonic acid are preferred.

[0070] Hereinafter, the dispersant as disclosed in JP-A No. 2010-106268, which is useful for the present invention will be described. A preferable dispersant is a graft copolymer having

a number of atoms excluding hydrogen atoms of from 40 to 10,000, and having a graft chain selected from a polyester structure, a polyether structure and a polyacrylate structure, and preferably contains a structural unit represented by at least one of the following Formulae (a) to (d), more preferably, contains a structural unit represented by any one of the following Formula (1A), the following Formula (2A), the following formula (3A), the following Formula (3B), or the following Formula (d).

[0071]

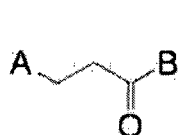


[0072] In Formulae (a) to (d), W^1 , W^2 , W^3 and W^4 each independently represent an oxygen atom or NH, and particularly preferably an oxygen atom.

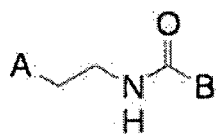
In Formulae (a) to (d), X^1 , X^2 , X^3 , X^4 and X^5 each independently represent a hydrogen atom or a monovalent organic group. From the viewpoint of synthetic restrictions, X^1 , X^2 , X^3 , X^4 and X^5 are each preferably a hydrogen atom or an alkyl group having 1 to 12 carbon atoms, more preferably a hydrogen atom or a methyl group, and particularly preferably a methyl group.

In Formulae (a) to (d), Y^1 , Y^2 , Y^3 and Y^4 each independently represent a divalent linking group, and have no particular structural restriction. Specific examples of the divalent linking group represented by Y^1 , Y^2 , Y^3 or Y^4 include the following linking groups (Y-1) to (Y-21). In the following structures (Y-1) to (Y-21), A indicates a bond between Y^1 and W^1 , Y^2 and W^2 , Y^3 and W^3 , and Y^4 and W^4 , respectively, in Formulae (a) to (d), and B indicates a bond between Y^1 , Y^2 , Y^3 , Y^4 and the moieties that are present at the opposite position with respect to W^1 , W^2 , W^3 , W^4 , respectively, in Formulae (a) to (b). Among the following structures, (Y-2) and (Y-13) are preferred in terms of synthesis simplicity.

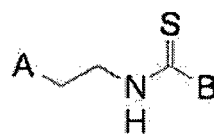
[0073]



(Y-1)



(Y-2)



(Y-3)



(Y-4)



(Y-5)



(Y-6)



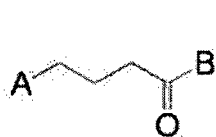
(Y-7)



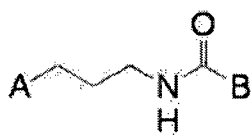
(Y-8)



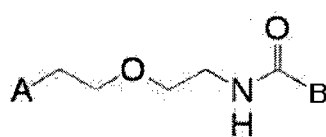
(Y-9)



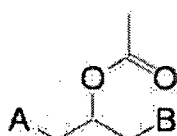
(Y-10)



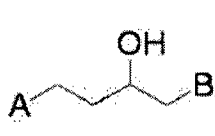
(Y-11)



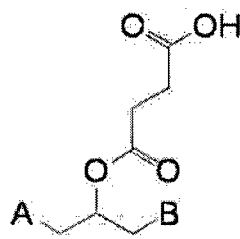
(Y-12)



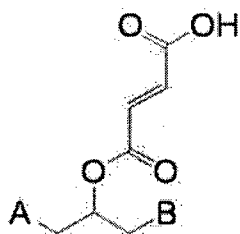
(Y-13)



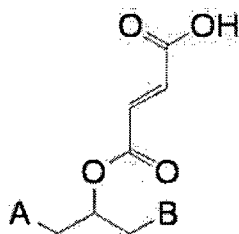
(Y-14)



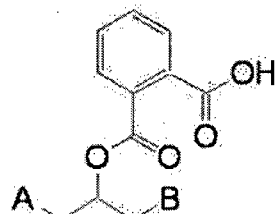
(Y-15)



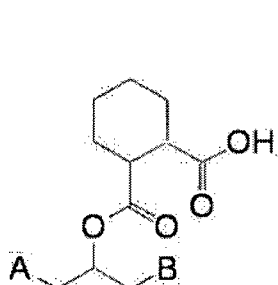
(Y-16)



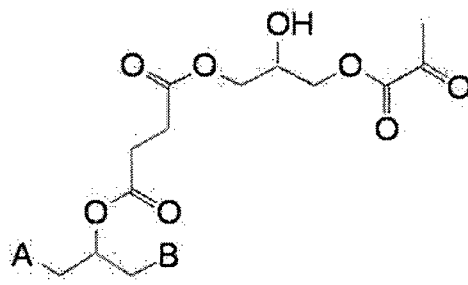
(Y-17)



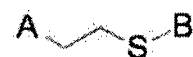
(Y-18)



(Y-19)



(Y-20)



(Y-21)

[0074] In Formulae (a) to (d), Z¹, Z², Z³ and Z⁴ each independently represent a monovalent

organic group and have no particular structural restriction. Specific examples of Z^1 , Z^2 , Z^3 and Z^4 include an alkyl group, a hydroxyl group, an alkoxy group, an aryloxy group, a heteroaryloxy group, an alkylthioether group, an arylthioether group, a heteroarylthioether group, and an amino group. Of these, monovalent organic groups represented by Z^1 , Z^2 , Z^3 and Z^4 preferably have steric hindrance effects from the viewpoint of improvement of dispersibility. The organic groups represented by Z^1 to Z^3 each independently represent an alkyl group having 5 to 24 carbon atoms or an alkoxy group having 5 to 24 carbon atoms, preferably each independently represent an alkoxy group having a branched alkyl group and having 5 to 24 carbon atoms or an alkoxy group having a cyclic alkyl group and having 5 to 24 carbon atoms. In addition, the organic groups represented by Z^4 each independently preferably represents an alkyl group having 5 to 24 carbon atoms, and in particular, each independently preferably a branched alkyl group having 5 to 24 carbon atoms or a cyclic alkyl group having 5 to 24 carbon atoms.

In Formula (a) to Formula (d), n, m, p and q each independently represent an integer of 1 to 500.

In Formulae (a) and (b), j and k each independently represent an integer of 2 to 8. In Formula (a) and Formula (b), j and k are preferably an integer of 4 to 6 from the viewpoints of dispersion stability and developability, and are most preferably 5.

[0075] In Formula (c), R^3 represents a branched or straight chain alkylene group. In Formula (c), R^3 is preferably an alkylene group having 1 to 10 carbon atoms, and more preferably an alkylene group having 2 to 3 carbon atoms.

In Formula (d), R^4 represents a hydrogen atom or a monovalent organic group and the monovalent organic group has no particular structural restriction. In Formula (d), R^4 is preferably a hydrogen atom, an alkyl group, an aryl group or a heteroaryl group, and more preferably a hydrogen atom or an alkyl group. In a case in which, in Formula (d), R^4 is an alkyl group, the alkyl group is preferably a straight chain alkyl group having 1 to 20 carbon atoms, a branched alkyl group having 3 to 20 carbon atoms, or a cyclic alkyl group having 5 to 20 carbon atoms, more preferably a straight chain alkyl group having 1 to 20 carbon atoms, and particularly preferably a straight chain alkyl group having 1 to 6 carbon atoms. In Formula (d), when plural R^4 's are present in a graft copolymer, plural R^4 's may be the same as or different from one another.

[0076] In the graft copolymer, the structural unit represented by any one of Formulae (a) to (d) is preferably present in an amount of 10% to 90 by mass%, and more preferably 30% to 70% by mass, based on the total mass of the graft copolymer. When the structural unit represented by any one of Formulae (a) to (d) is present in an amount within the above ranges,

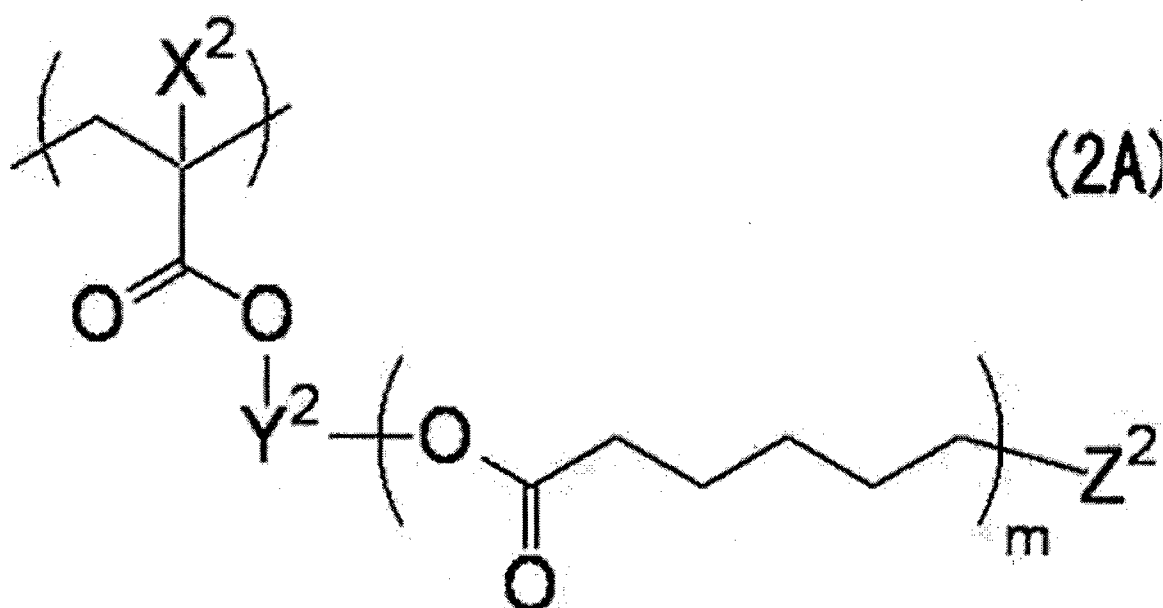
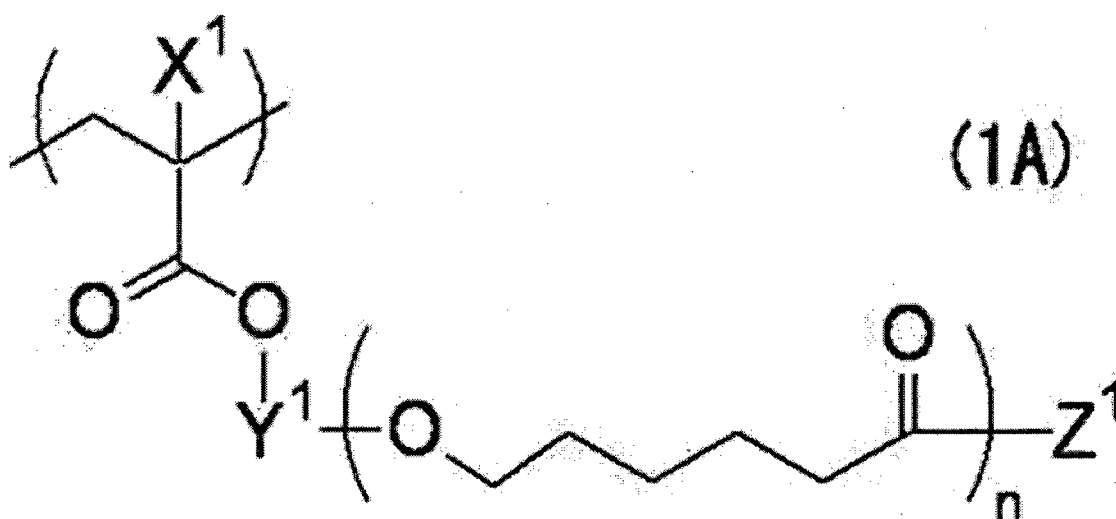
dispersibility of the pigment is high and developability is excellent during formation of a light-shielding film.

[0077] In addition, two or more graft copolymers that have different structures from one another may be present.

[0078] The structural unit represented by Formula (a) is more preferably a structural unit represented by the following Formula (1A) from the viewpoints of dispersion stability and developability.

In addition, the structural unit represented by Formula (b) is more preferably a structural unit represented by the following Formula (2A) from the viewpoints of dispersion stability and developability.

[0079]

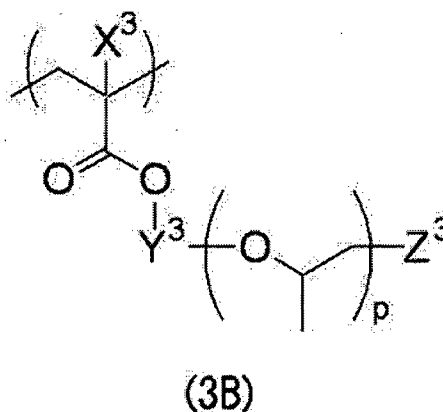
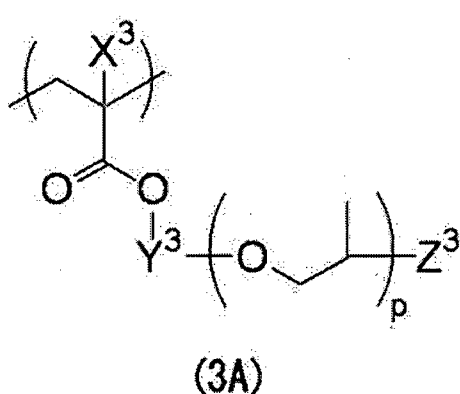


[0080] X^1 , Y^1 , Z^1 and n in Formula (1A) have the same definitions as X_1 , Y^1 , Z^1 and n in Formula (a), respectively, and preferable ranges (including preferable examples) thereof are also the same.

X^2 , Y^2 , Z^2 and m in Formula (2A) have the same definitions as X^2 , Y^2 , Z^2 and m in Formula (b), respectively, and preferable ranges (including preferable example) thereof are also the same.

The structural unit represented by Formula (c) is more preferably a structural unit represented by the following Formula (3A) or the following Formula (3B) from the viewpoints of dispersion stability and developability.

[0081]

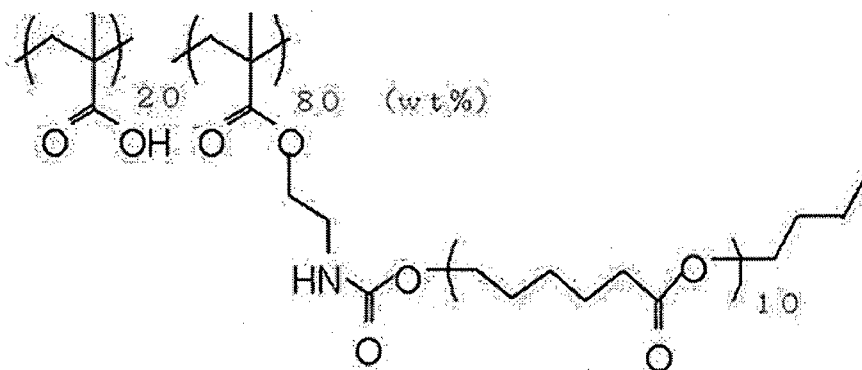


[0082] X^3 , Y^3 , Z^3 and p in Formula (3A) or (3B) have the same definitions as X^3 , Y^3 , Z^3 and p in formula (c), respectively, and preferable ranges (including preferable example) thereof are also the same.

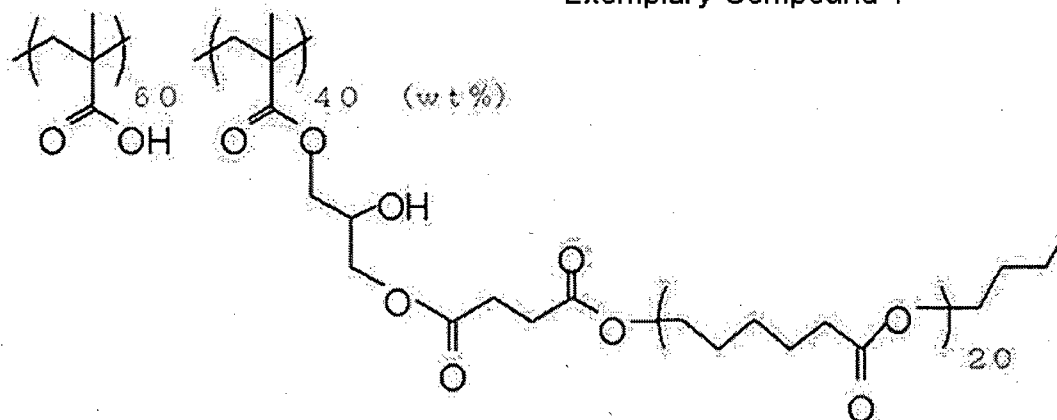
[0083] The graft copolymer is more preferably a structural unit represented by Formula (1A) mentioned above.

[0084] Specific examples of the graft copolymer include the following compounds. In the following exemplary compounds, the numerical value shown with respective structural units means the content of the corresponding structural unit [% by mass, arbitrarily referred to as "(wt%)"]. The numerical values recited beside the repeating units of side chains each indicate the repetition number of the repeating unit.

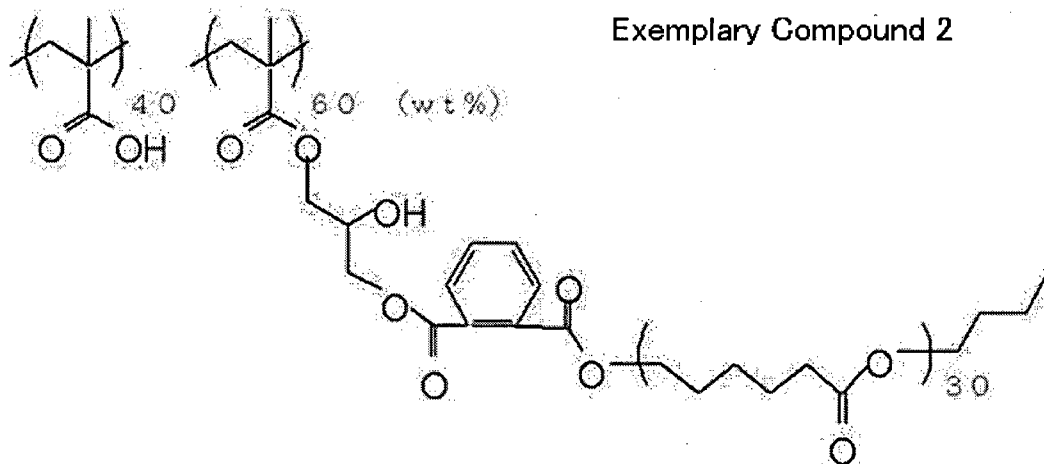
[0085]



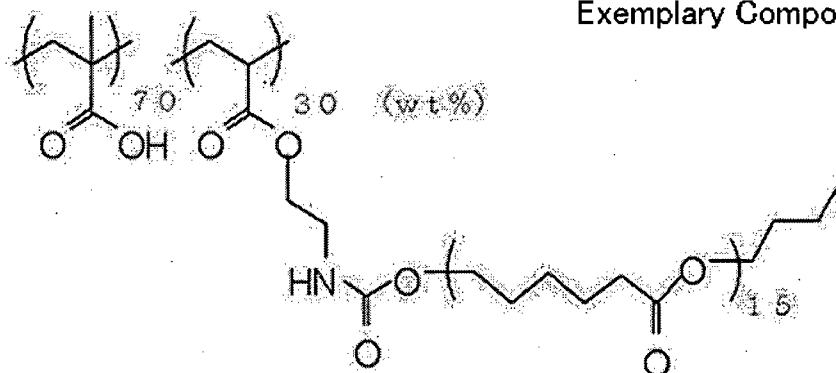
Exemplary Compound 1



Exemplary Compound 2

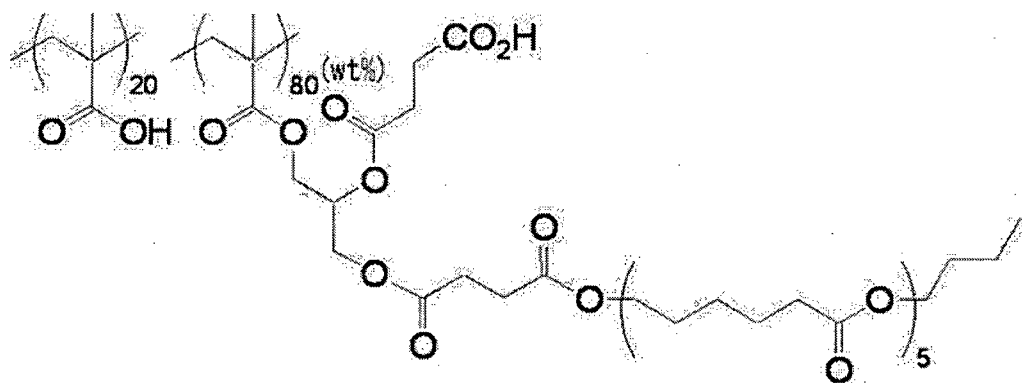


Exemplary Compound 3

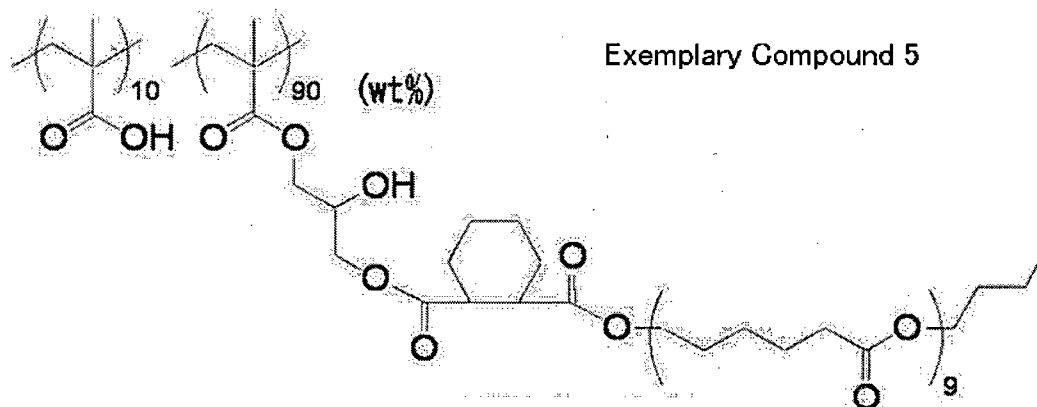


Exemplary Compound 4

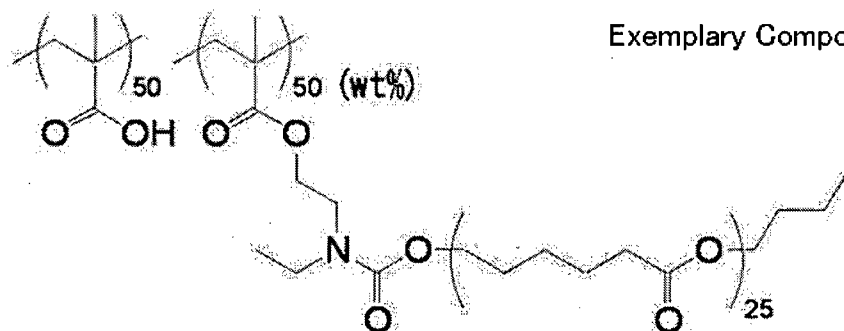
[0086]



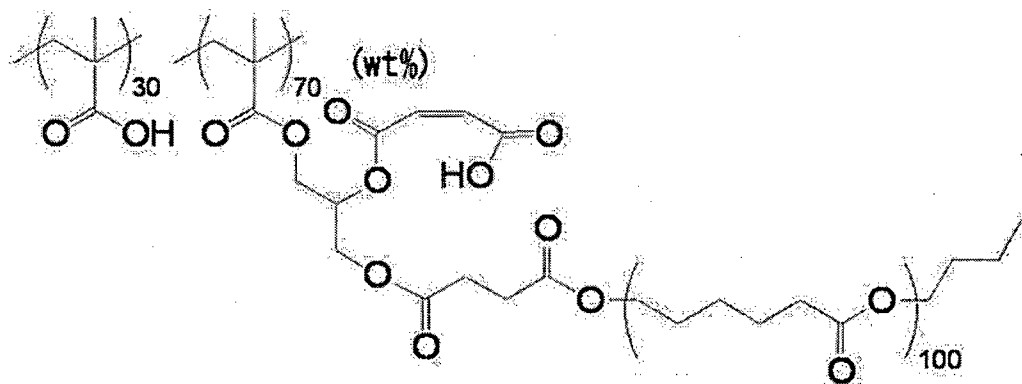
Exemplary Compound 5



Exemplary Compound 6

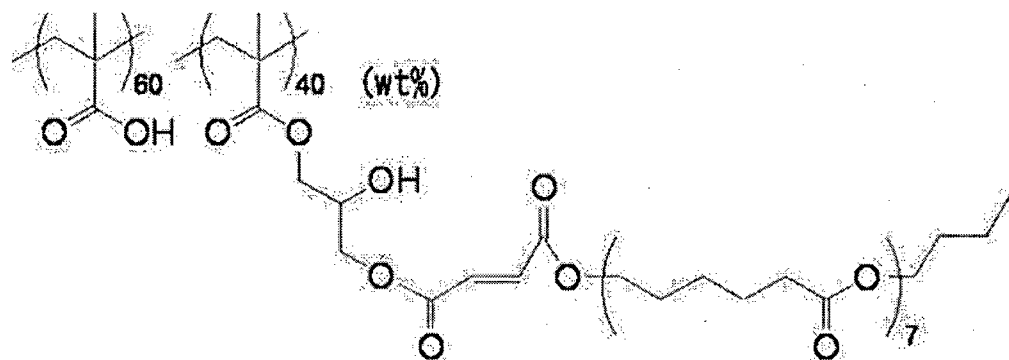


Exemplary Compound 7

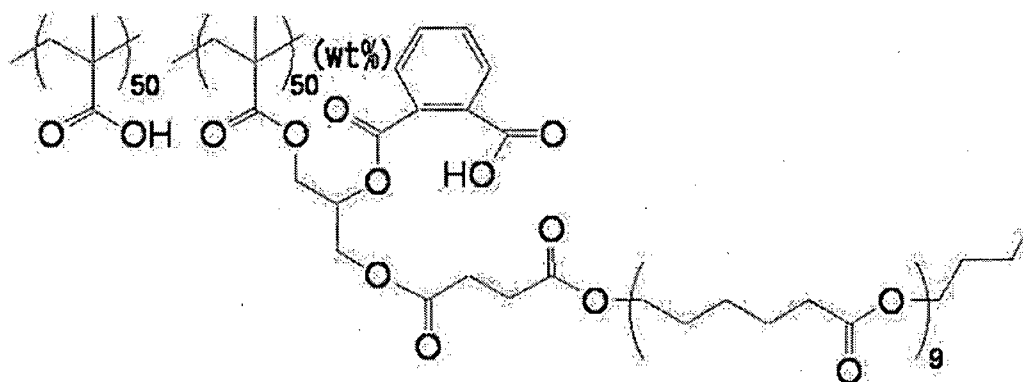


Exemplary Compound 8

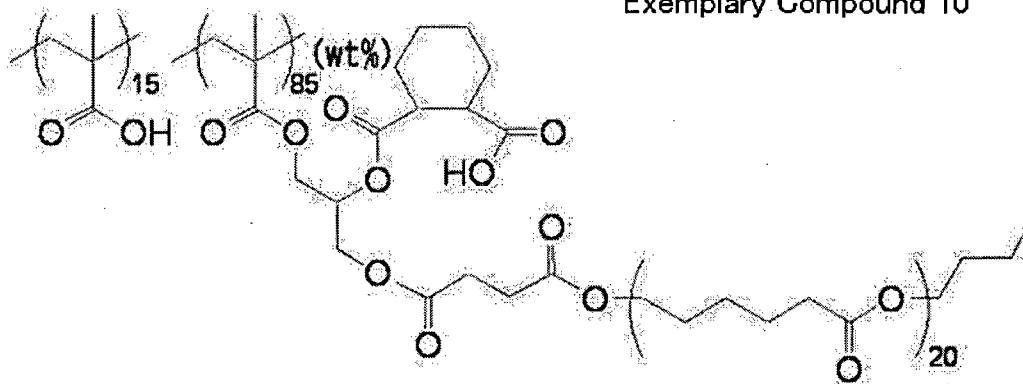
[0087]



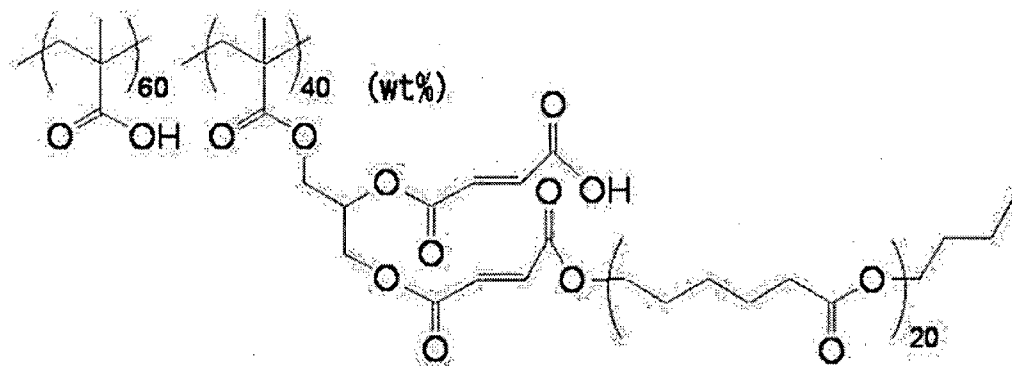
Exemplary Compound 9



Exemplary Compound 10

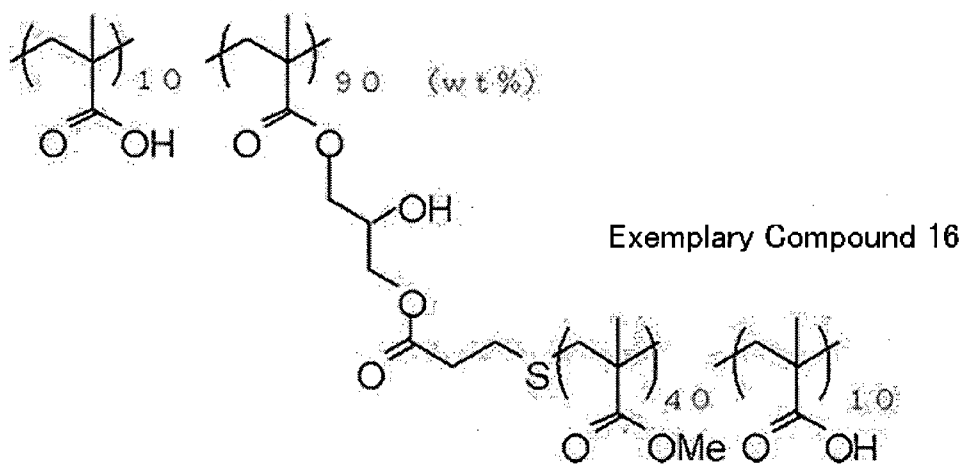
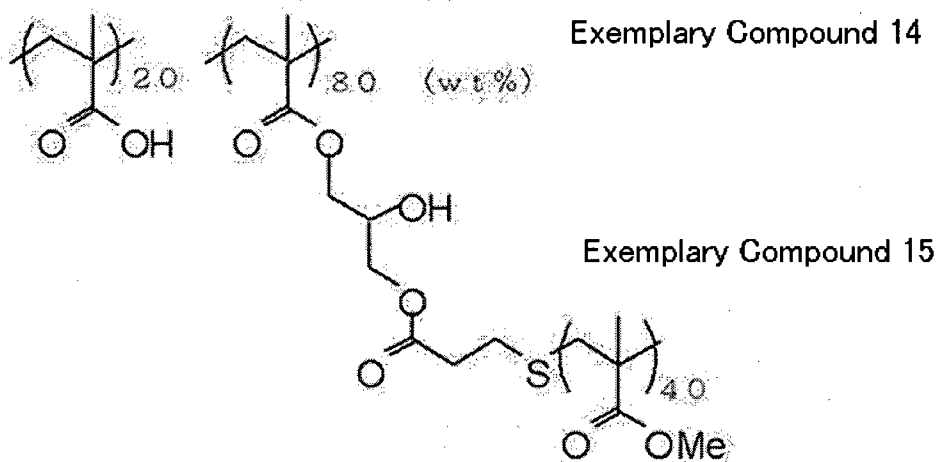
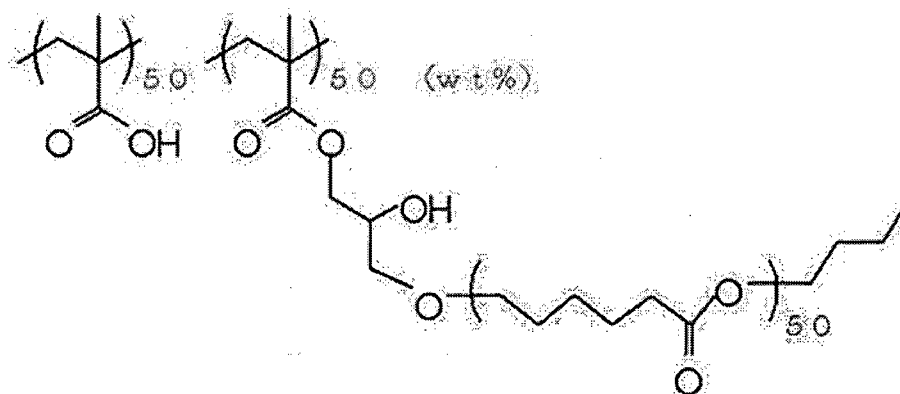
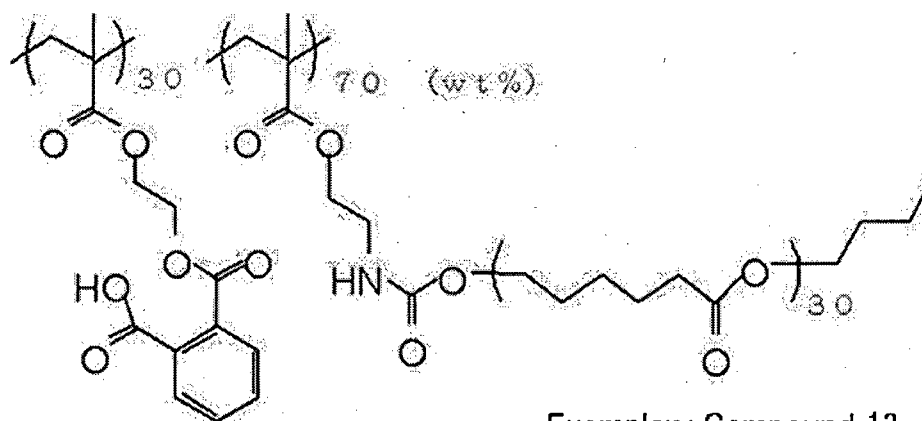


Exemplary Compound 11

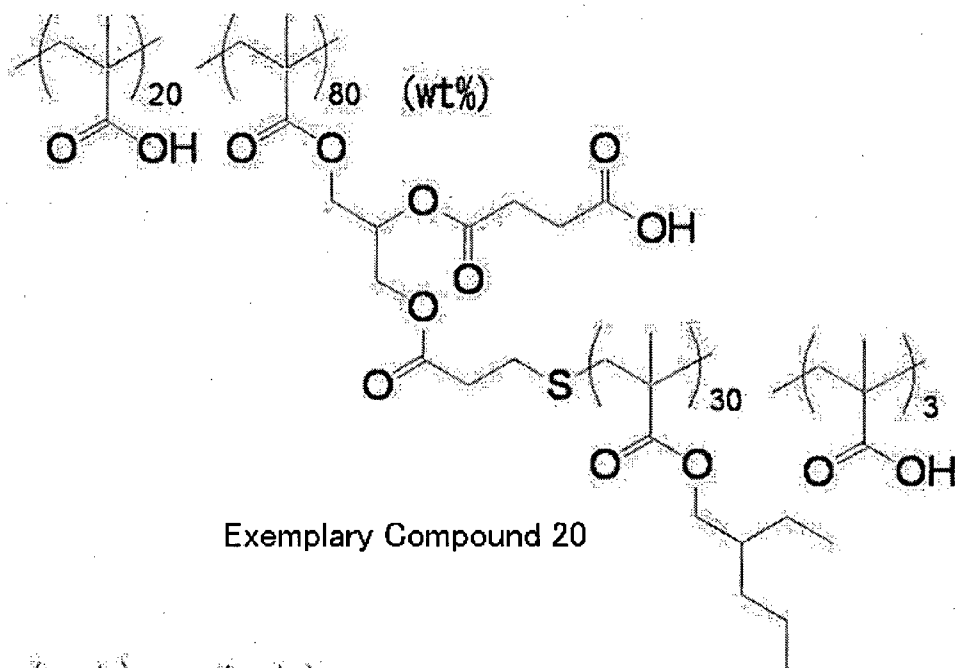


Exemplary Compound 12

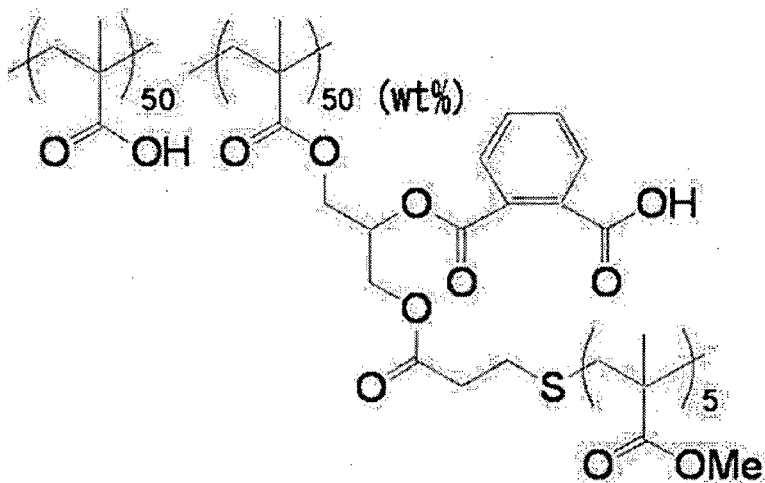
[0088]



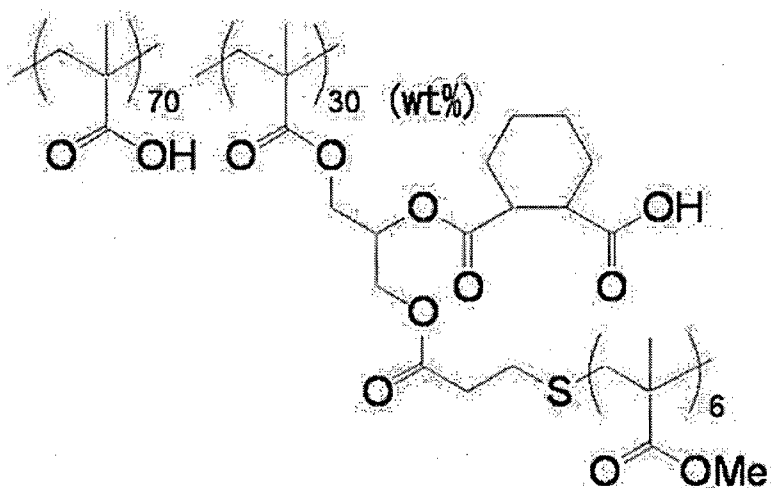
[0089]



Exemplary Compound 20

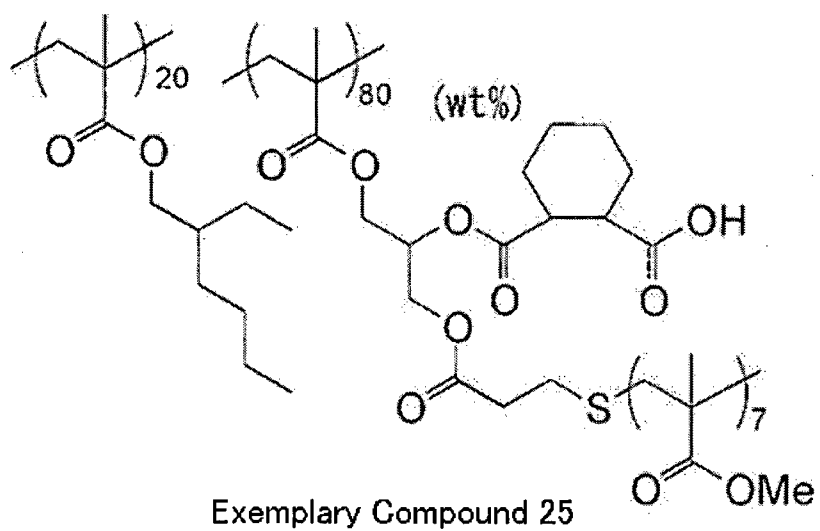
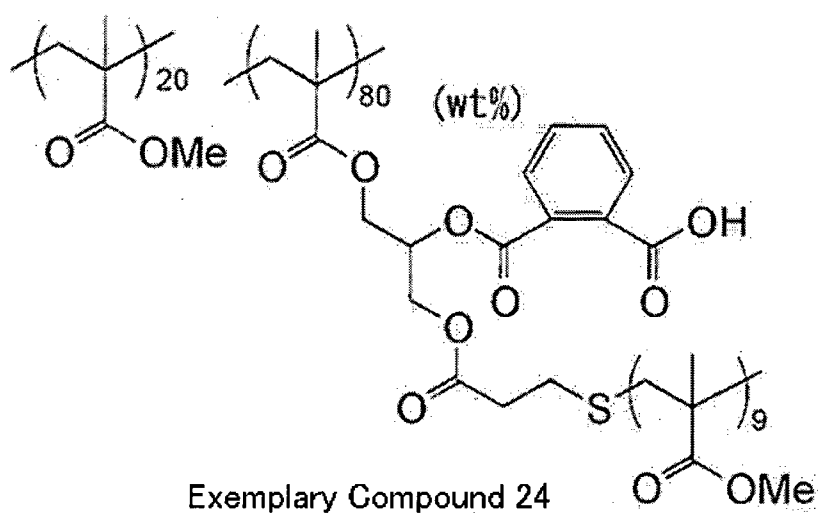
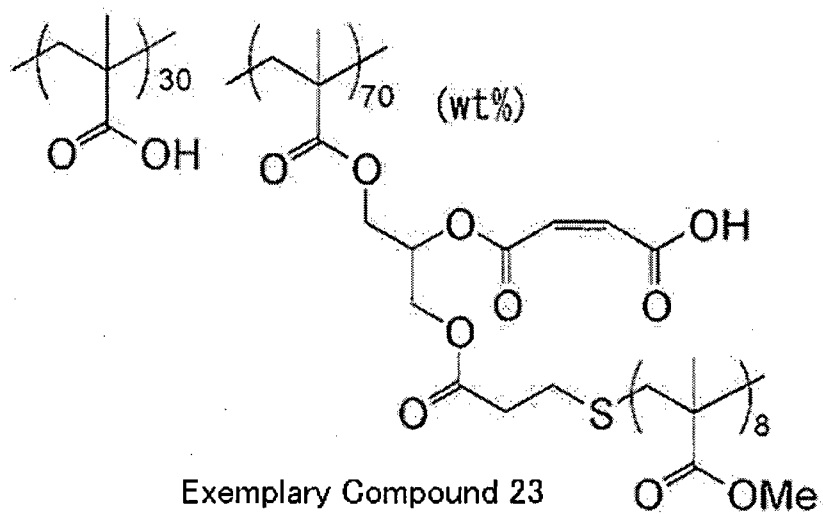


Exemplary Compound 21

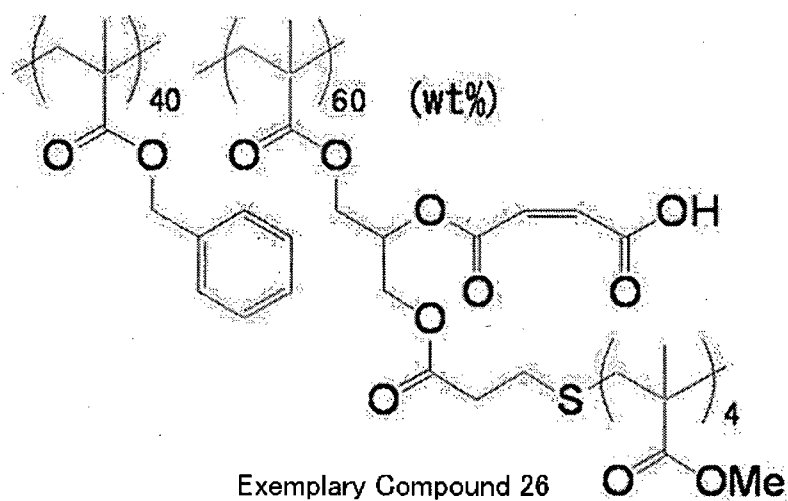


Exemplary Compound 22

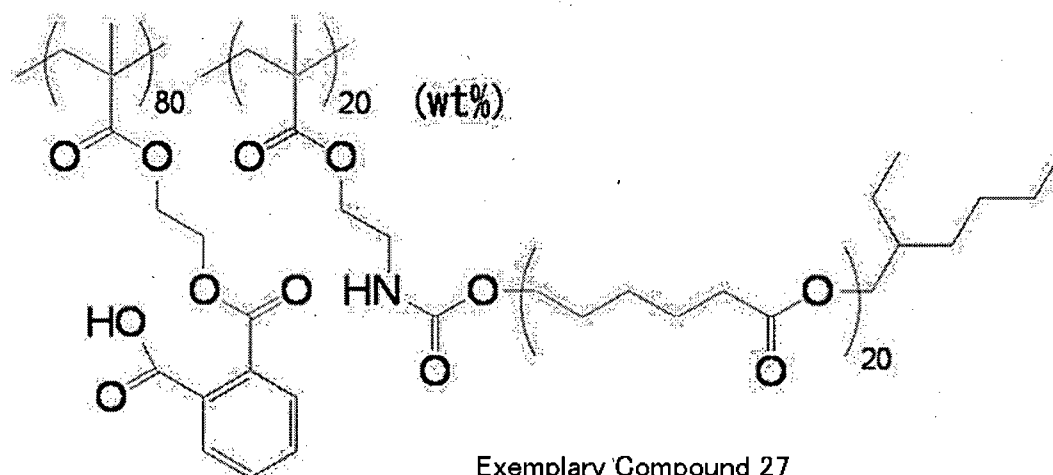
[0090]



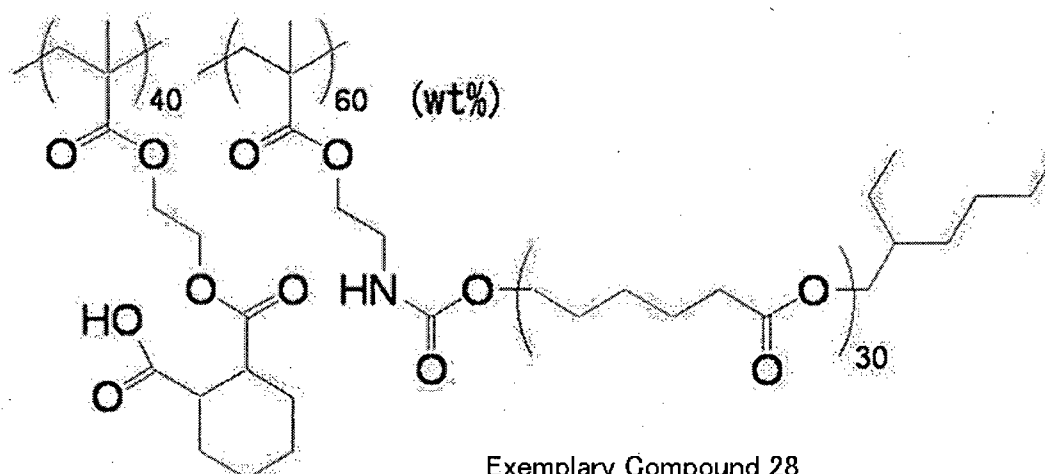
[0091]



Exemplary Compound 26

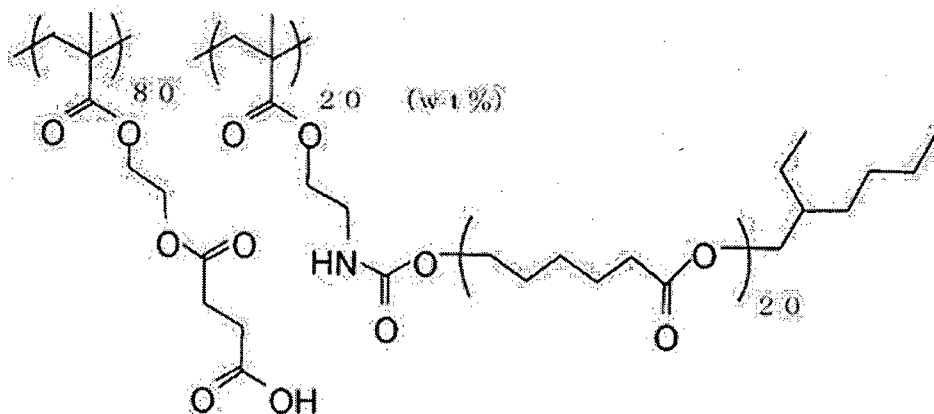


Exemplary Compound 27

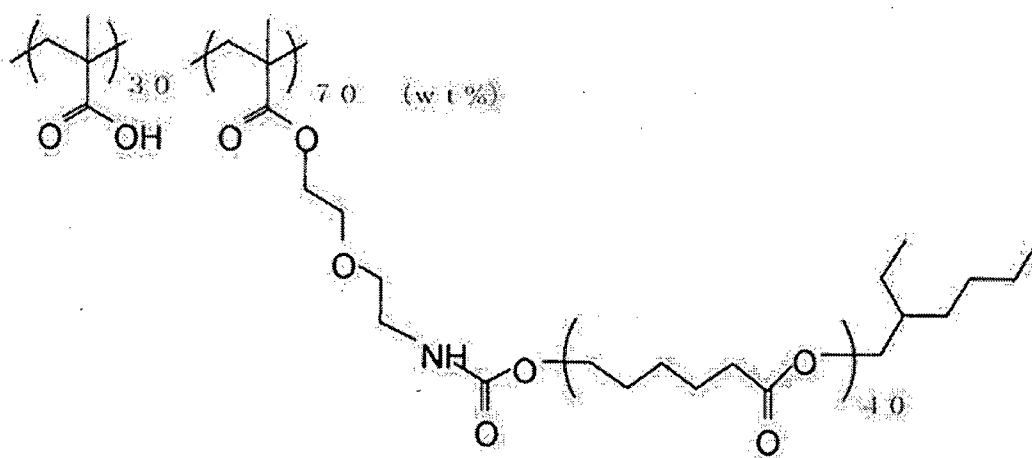


Exemplary Compound 28

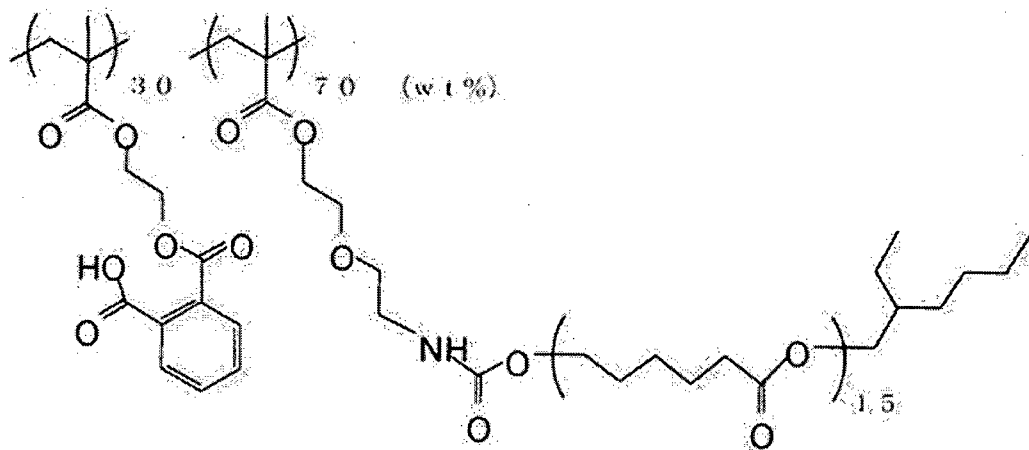
[0092]



Exemplary Compound 29

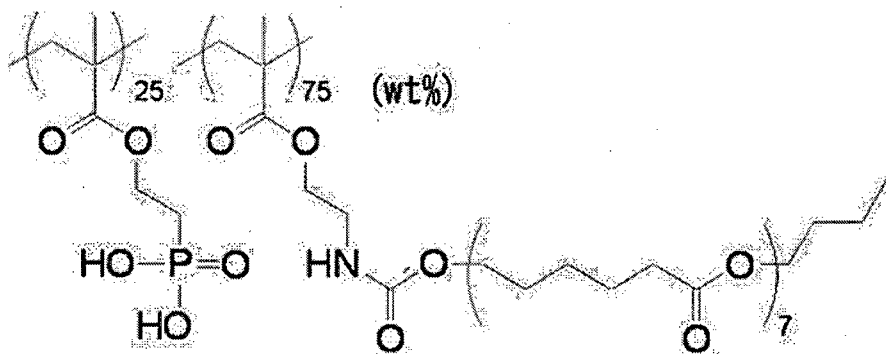


Exemplary Compound 30

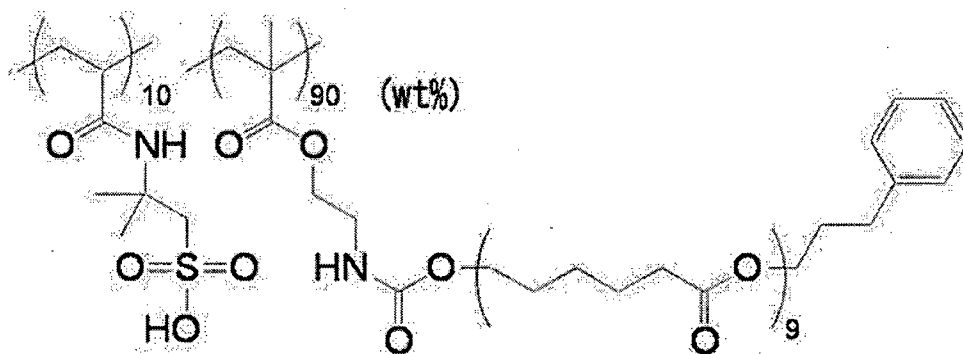


Exemplary Compound 31

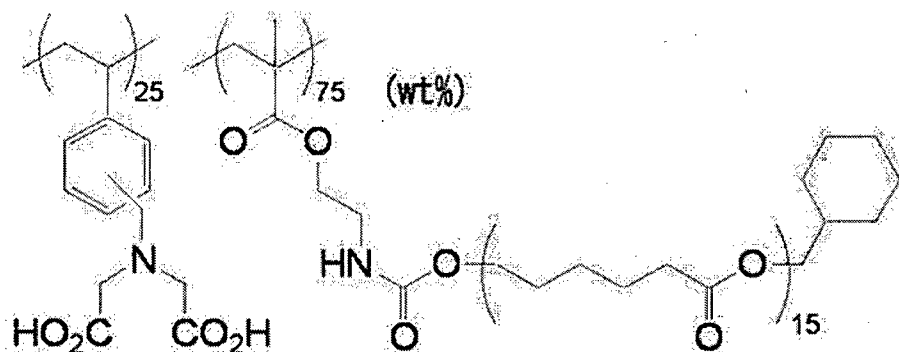
[0093]



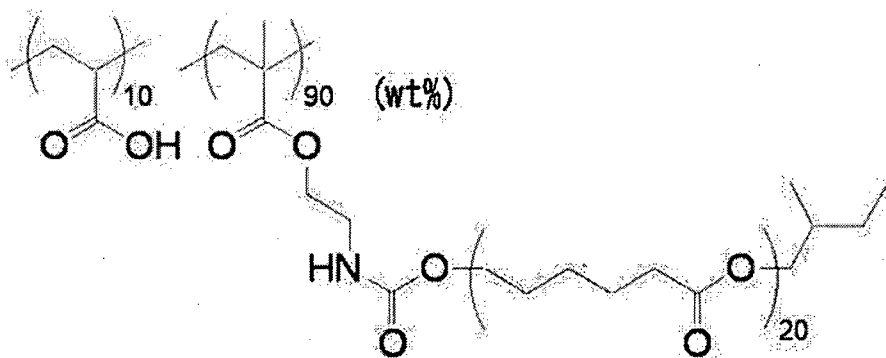
Exemplary Compound 32



Exemplary Compound 33

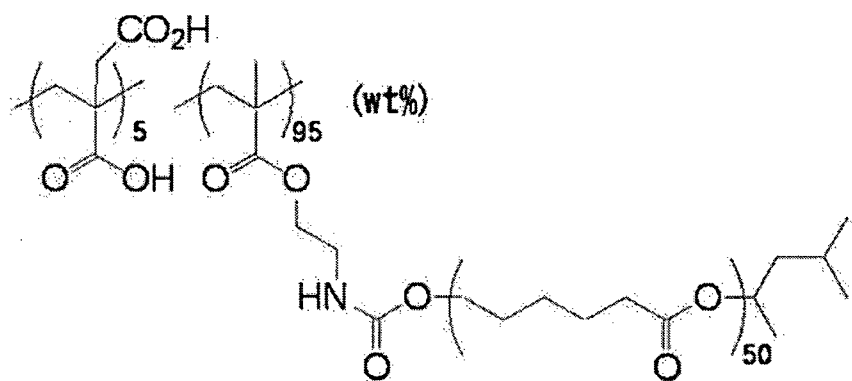


Exemplary Compound 34

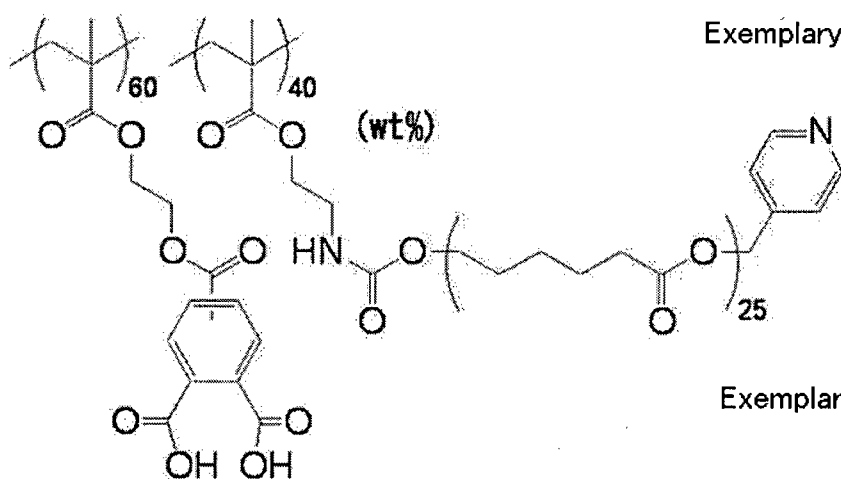


Exemplary Compound 35

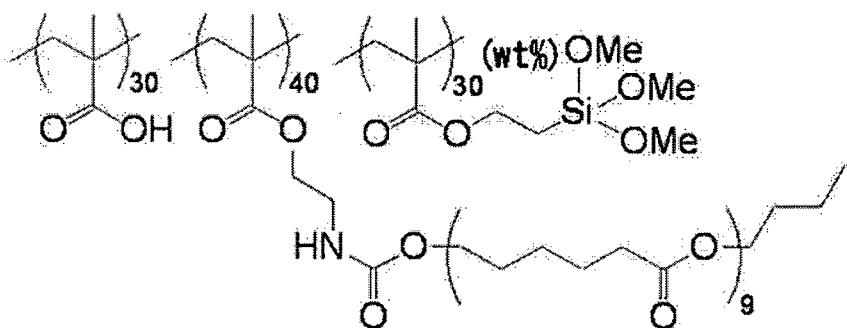
[0094]



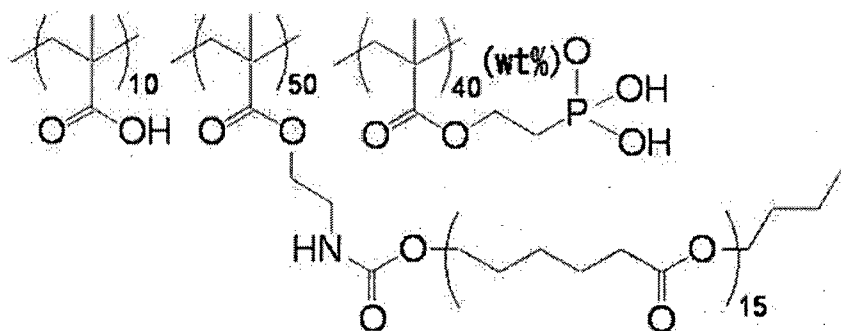
Exemplary Compound 36



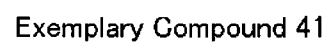
Exemplary Compound 37



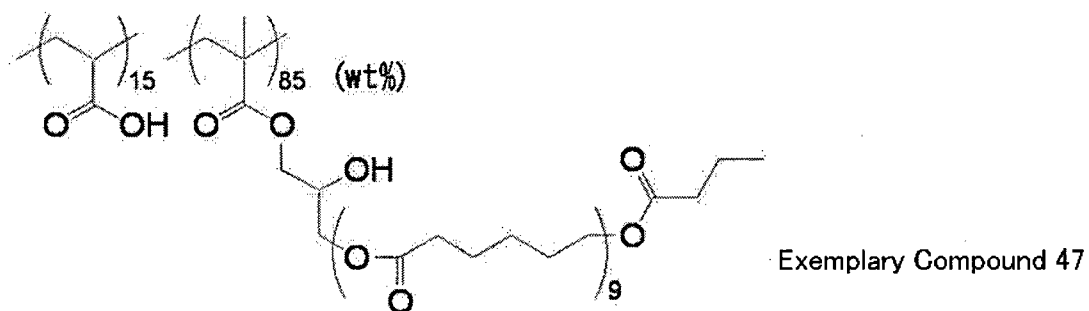
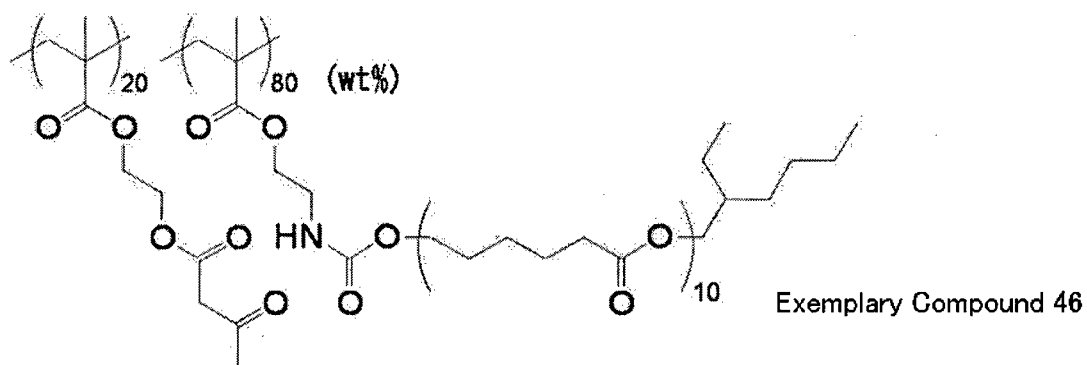
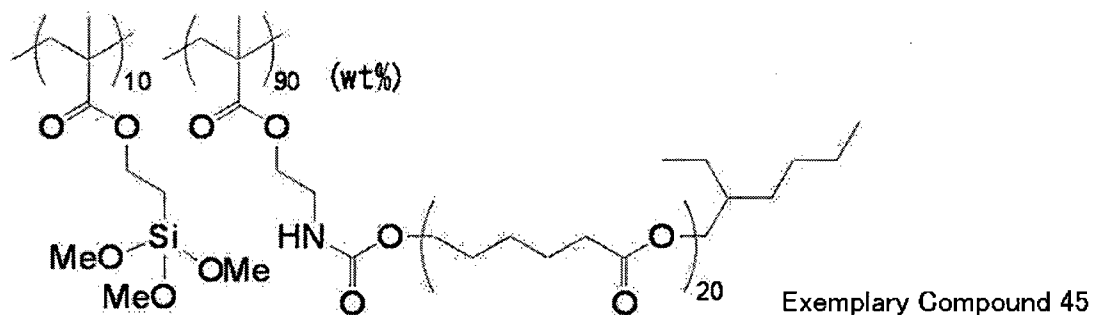
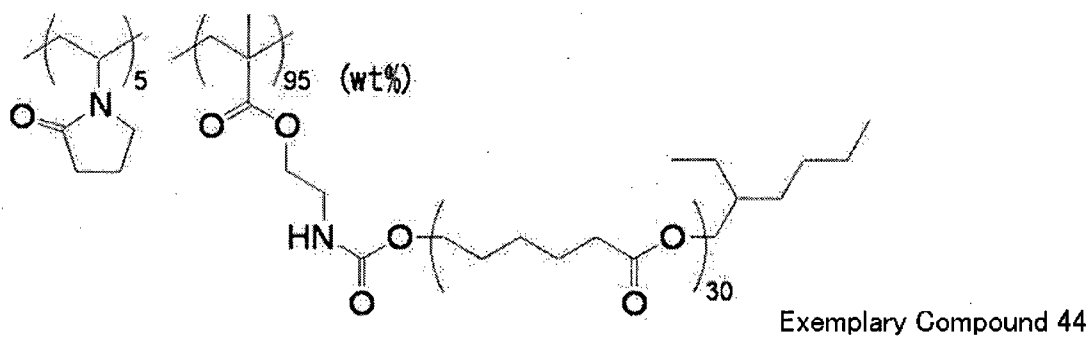
Exemplary Compound 38



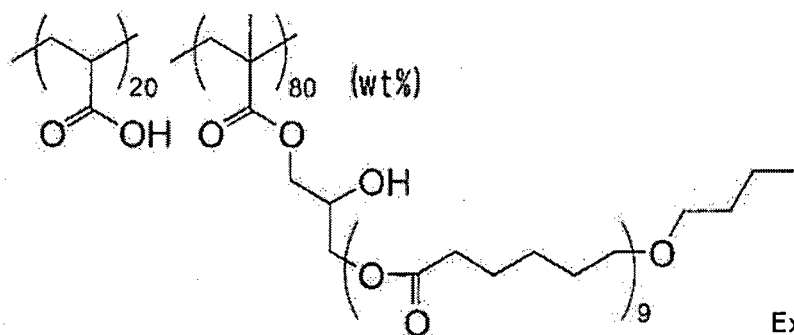
Exemplary Compound 39



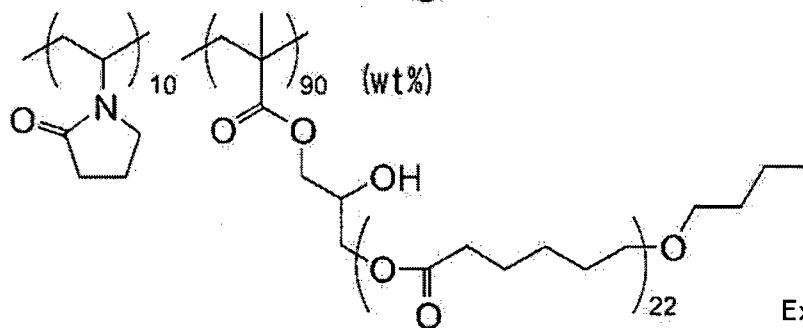
[0096]



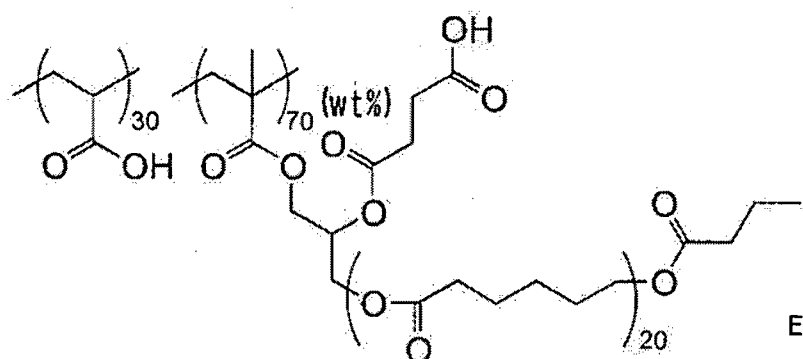
[0097]



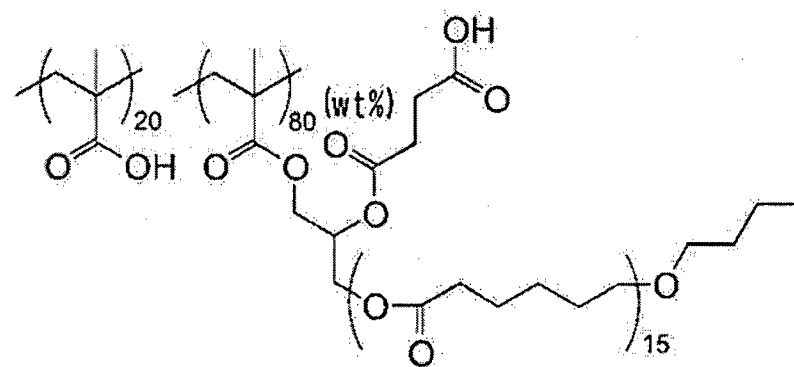
Exemplary Compound 48



Exemplary Compound 49

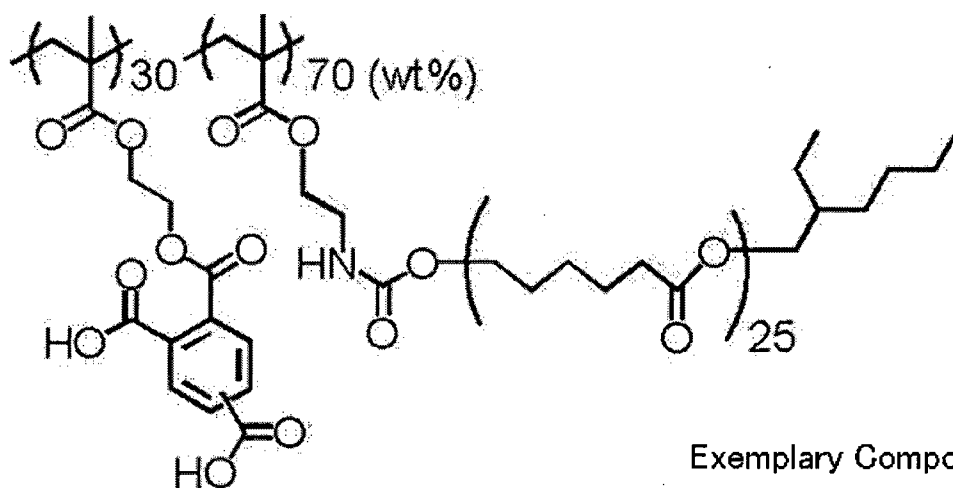


Exemplary Compound 50



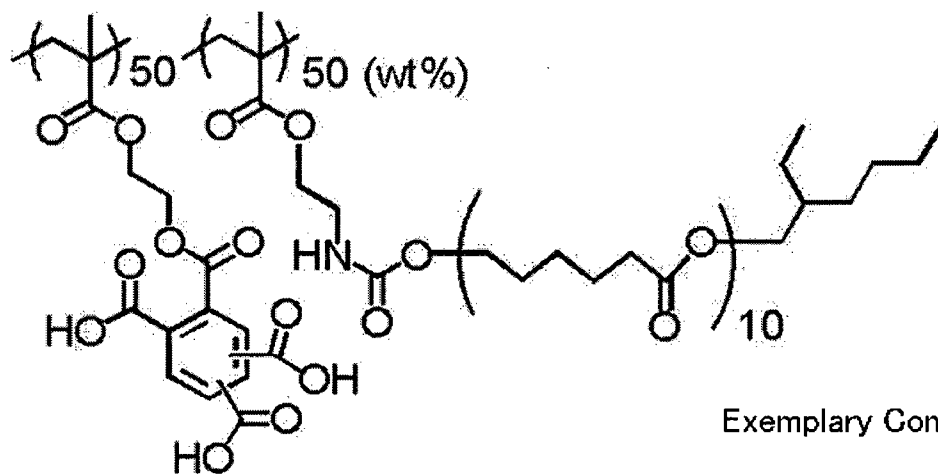
Exemplary Compound 51

[0098]



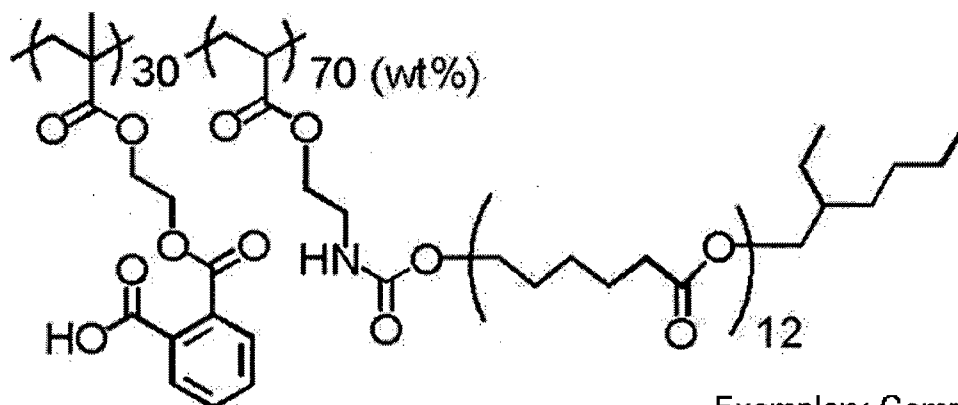
Exemplary Compound 52

[0099]



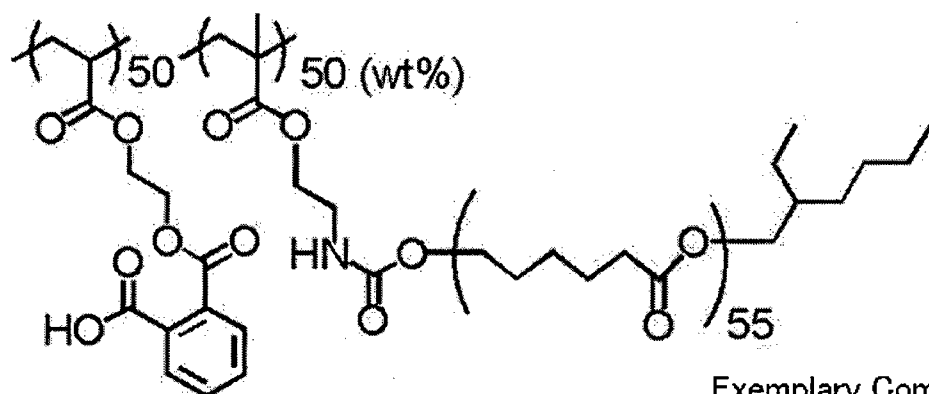
Exemplary Compound 53

[0100]



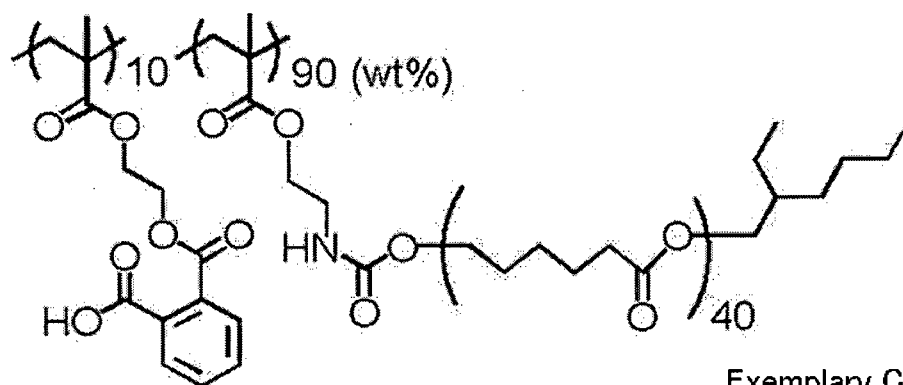
Exemplary Compound 54

[0101]



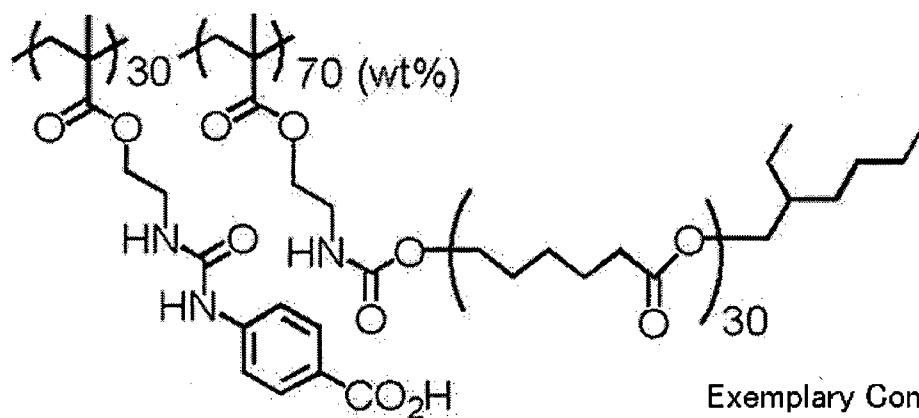
Exemplary Compound 55

[0102]



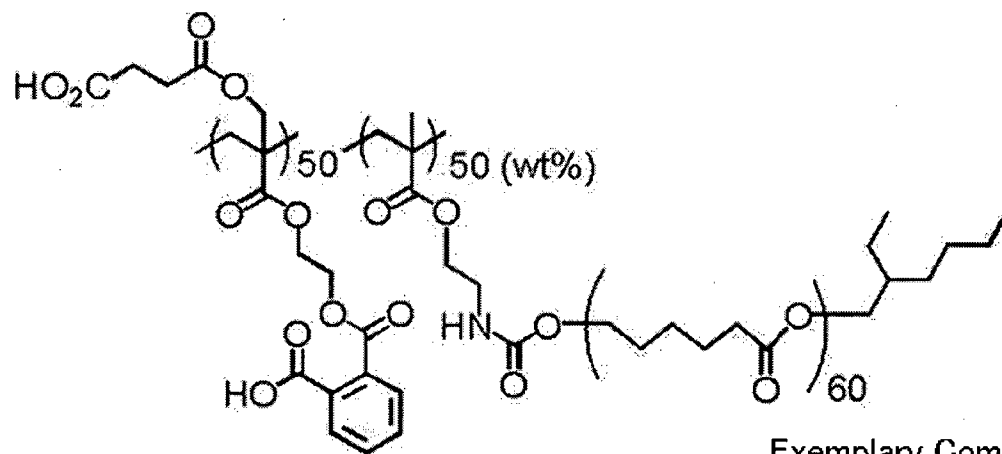
Exemplary Compound 56

[0103]



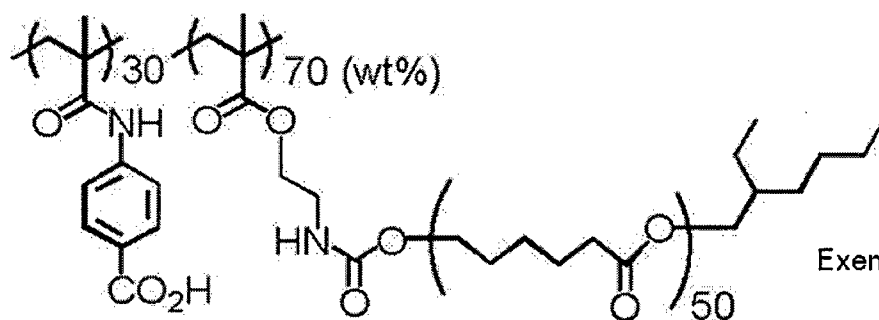
Exemplary Compound 57

[0104]



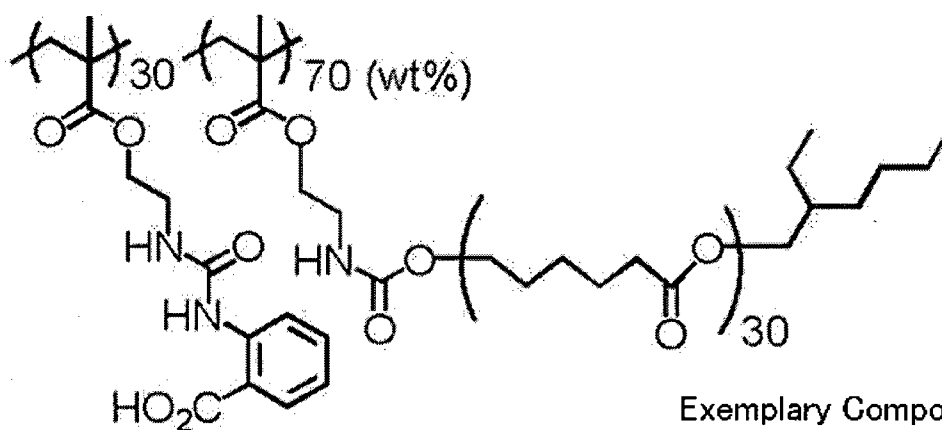
Exemplary Compound 58

[0105]



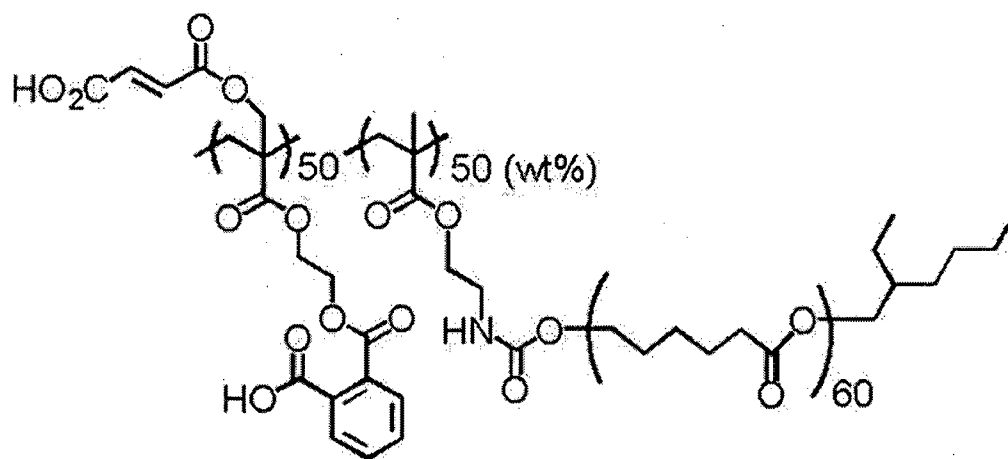
Exemplary Compound 59

[0106]



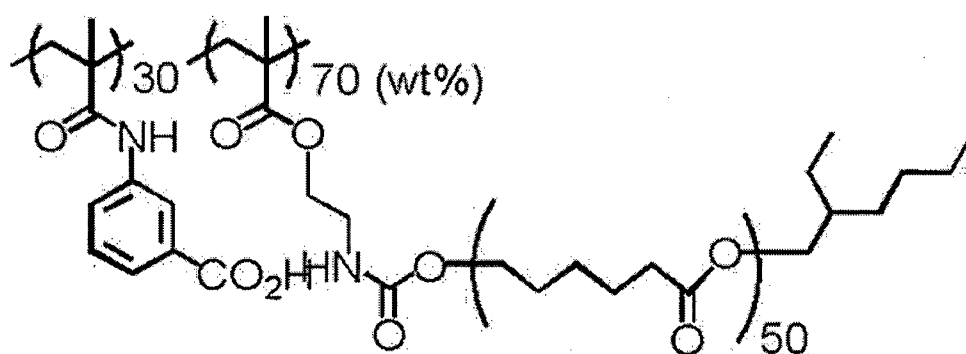
Exemplary Compound 60

[0107]



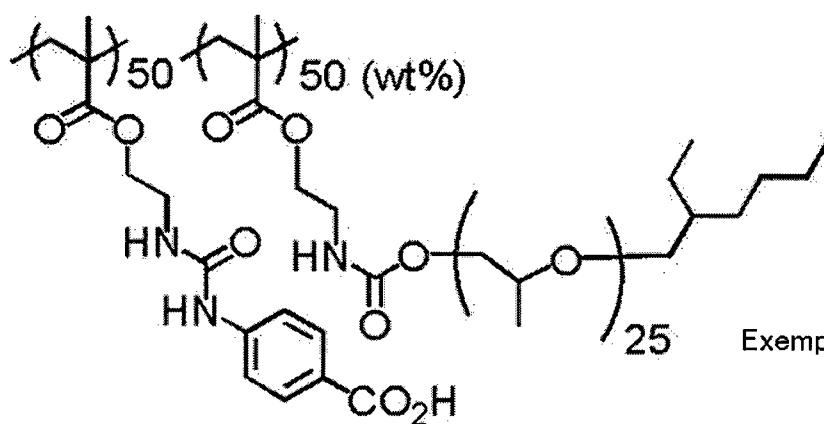
Exemplary Compound 61

[0108]



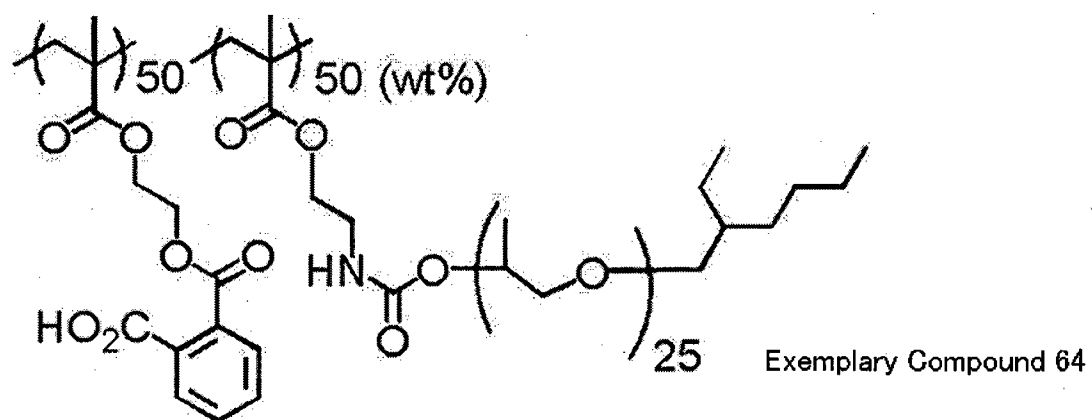
Exemplary Compound 62

[0109]

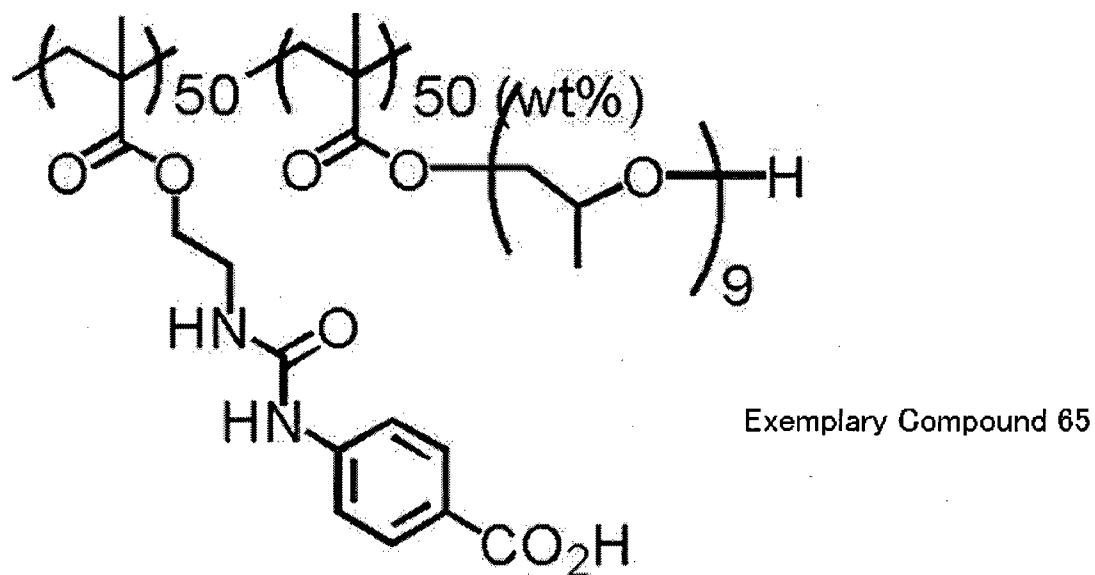


Exemplary Compound 63

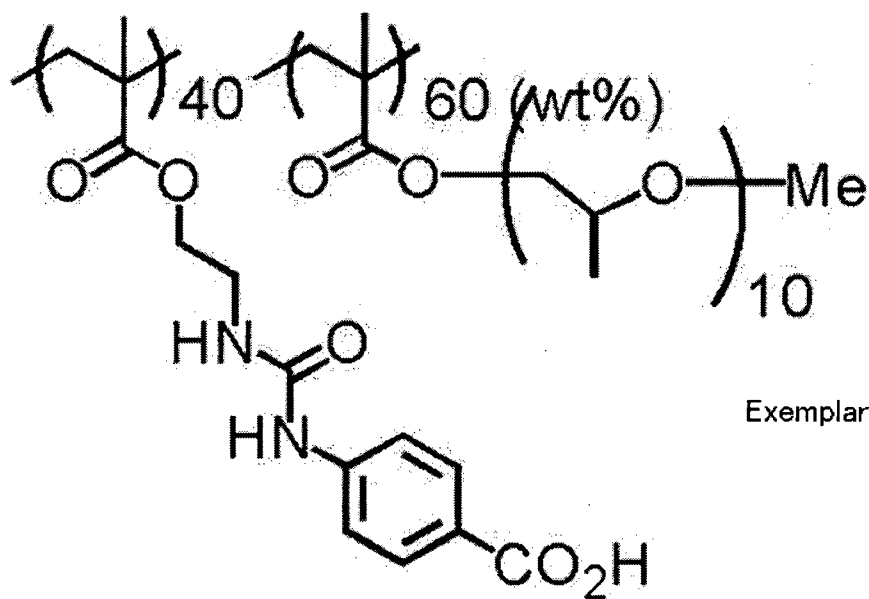
[0110]



[0111]

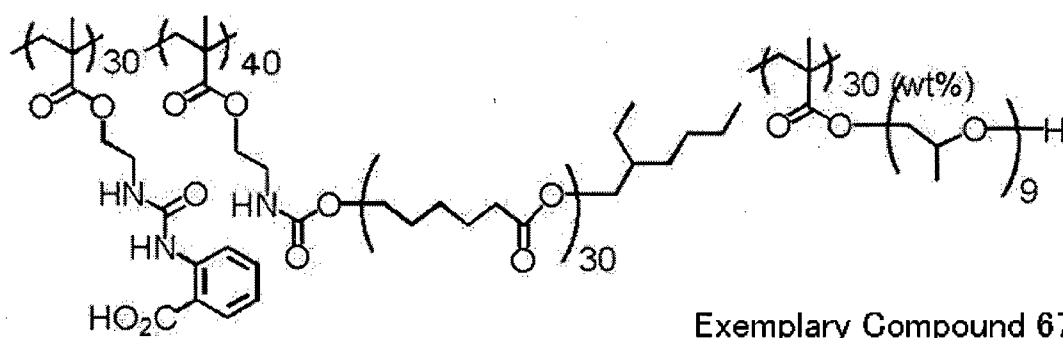


[0112]



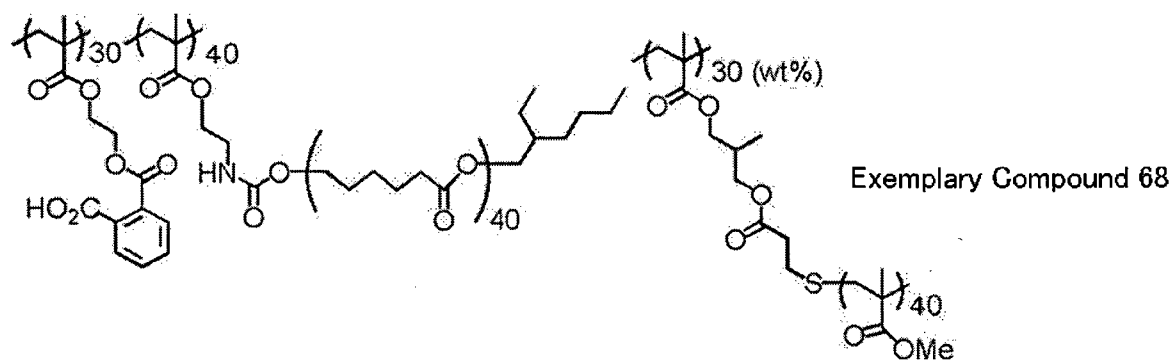
Exemplary Compound 66

[0113]



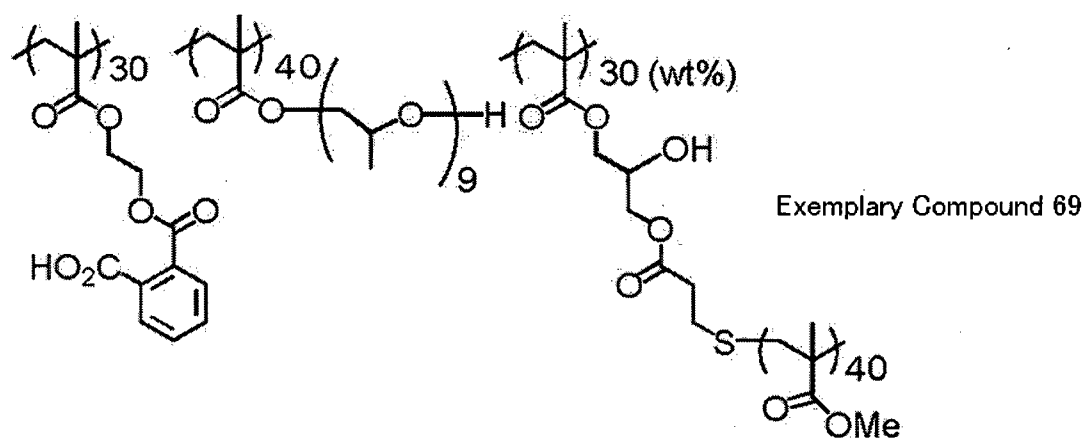
Exemplary Compound 67

[0114]

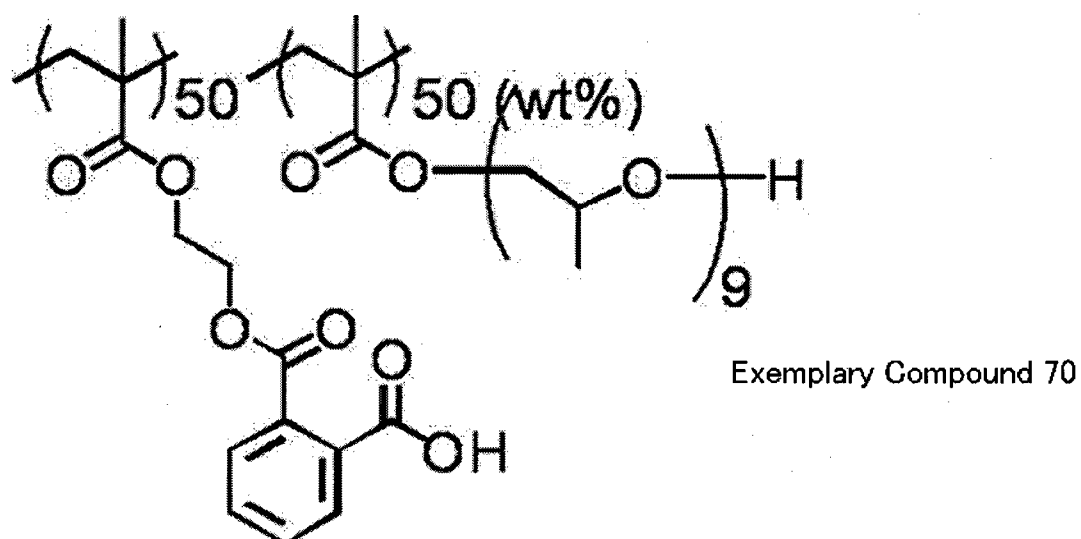


Exemplary Compound 68

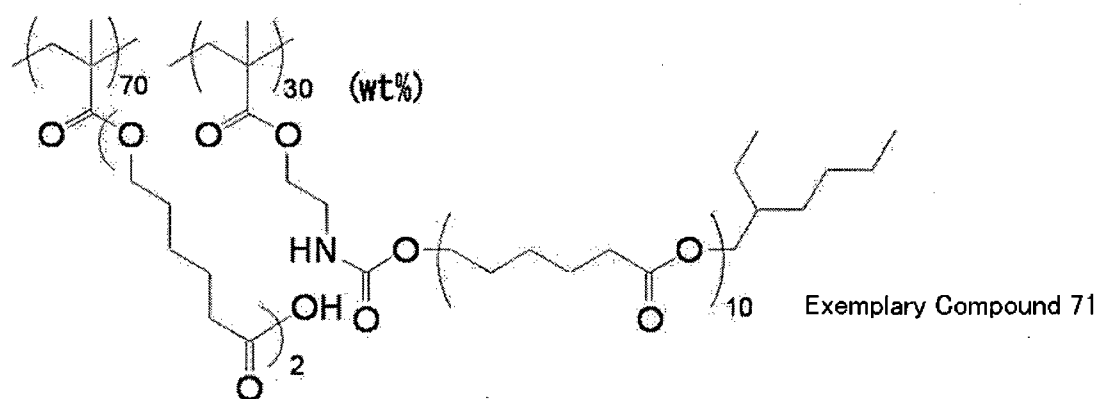
[0115]



[0116]



[0117]





$$\begin{array}{c} \text{---} \left(\text{CH}_2 \right)_4 \text{CH} \left(\text{COOCH}_2\text{CH}_2\text{O} \left(\text{CH}_2 \right)_6 \text{COO} \right)_n \text{CH} \left(\text{CH}_2 \right)_4 \text{---} \\ \text{80} \end{array}$$

The content of the (B) first filler in the filler dispersion (i.e., first filler dispersion) is preferably 0.1% by mass to 5% by mass, more preferably 0.1 % by mass to 3% by mass, and most preferably 0.1% by mass to 2% by mass. When the content is higher than the upper limit of the above ranges, dispersion stability of particles is deteriorated over time, and when

the content is lower than the lower limit of the above ranges, the thickness uniformity on uneven surface, effect of the present invention is slightly deteriorated.

The content of the (C) second filler in the filler dispersion (i.e., second filler dispersion) is preferably 1% by mass to 20% by mass, more preferably 1% by mass to 15% by mass, and most preferably 1% by mass to 10% by mass. When the content is higher than the upper limit of the above ranges, dispersion stability of particles is deteriorated over time, and when the content is lower than the lower limit of the above ranges, thickness uniformity on uneven surface, the effect of the present invention is slightly deteriorated.

[0123] *Solvent*

The solvent which may be used for each particle dispersion and light-shielding composition is not particularly limited. Any solvent may be suitably selected according to the intended purpose so long as it is capable of uniformly dissolving or dispersing the respective components of the light-shielding composition of the present invention. Examples of useful solvents include alcohols such as methanol, ethanol, normal-propanol, isopropanol, normal-butanol, secondary-butanol, or normal-hexanol; ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, diisobutyl ketone, cyclohexanone, or cyclopentanone; esters such as ethyl acetate, butyl acetate, normal-amyl acetate, methyl sulfate, ethyl propionate, methyl phthalate, ethyl benzoate, propylene glycol monomethyl ether acetate, or methoxypropyl acetate; aromatic hydrocarbons such as toluene, xylene, benzene, or ethylbenzene; halogenated hydrocarbons such as carbon tetrachloride, trichloroethylene, chloroform, 1,1,1-trichloroethane, methylene chloride, or monochlorobenzene; ethers such as tetrahydrofuran, diethyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 1-methoxy-2-propanol, propylene glycol monomethyl ether, or dipropylene glycol monomethyl ether; and dimethylformamide, dimethylacetamide, dimethyl sulfoxide, and sulfolane.

Particularly preferred is 1-methoxy-2-propanol, propylene glycol monomethyl ether acetate, or dipropylene glycol monomethyl ether, and it is most preferable that the solvent contains propylene glycol monomethyl ether acetate.

The solvents may be used alone or in combination of two or more types thereof.

[0124] The content of light-shielding particle in the light-shielding particle-containing dispersion is preferably 30% by mass to 80% by mass, and more preferably 40% by mass to 70% by mass, with respect to the total solid content (mass) in the dispersion. When the content of light-shielding particle is within the above ranges, the light-shielding particles tends to be easily dispersed and stability of the obtained dispersion is excellent.

Regarding the content of (B) first filler in the dispersion containing a (B) first filler,

and the content of (C) second filler in the dispersion containing a (C) second filler, the content of (B) first filler is preferably 20% by mass to 70% by mass, more preferably 30% by mass to 50% by mass, with respect to the total solid (mass) in the filler dispersion containing a (B) first filler (i.e., the first filler dispersion), and the content of (C) second filler is preferably 3% by mass to 30% by mass, and more preferably 5% by mass to 20% by mass, with respect to the total solid (mass) in the filler dispersion containing a (C) second filler (i.e., the second filler dispersion). When the contents of the first and second fillers are within the above ranges, respectively, the fillers tend to be easily dispersed and stability of the obtained dispersions is good.

[0125] The content of dispersant in each of the particle dispersions is preferably 30% by mass to 80% by mass, and more preferably 40% by mass to 80% by mass, with respect to the mass of the light-shielding particle, (B) first filler, or (C) second filler contained in the particle dispersions, respectively. When the content of dispersant is within the above ranges, the particle tends to be easily dispersed and stability of the obtained dispersions is good.

[0126] It is preferable that the light-shielding composition of the present invention contains a dispersion of (A) any one of a light-shielding particle or a light-shielding dye, a dispersion of a (B) first filler and a dispersion of a (C) second filler, and further contains (D) a polymerizable compound, and (E) a photopolymerization initiator. When the light-shielding composition contains these components, the composition has a radiation sensitivity, and thus is capable of forming a pattern or having a curing property.

[0127] *(D) Polymerizable compound*

The light-shielding composition of the present invention preferably contains (D) a polymerizable compound.

The polymerizable compound used herein may be any compound that has, in a molecule, a functional group that is capable of reacting with at least one of acid, radicals or heat (in this specification, such a functional group may be referred to as "polymerizable group"). Preferably, the polymerizable compound is a multifunctional polymerizable compound that has plural polymerizable groups in a molecule thereof.

Examples of the polymerizable compound that has a functional group which is capable of reacting with at least one of acid, radicals or heat that is preferable for the present invention include ethylenically unsaturated group-containing compounds that contain an ethylenically unsaturated group such as an unsaturated ester functional group, an unsaturated amide group, a vinyl ether group or an allyl group; and methylol compounds, bismaleimide compounds, benzocyclobutene compounds, bis(allyl)nadimide compounds, and benzoxazine compounds.

[0128] Examples of polymerizable compounds that can be preferably used for the present invention include general radical polymerizable compounds, and compounds having an ethylenically unsaturated double bond well-known in the art may be used without particular limitation. For example, these compounds may have a chemical form such as a monomer, a prepolymer, that is, a dimer, a trimer and an oligomer or a mixture thereof and a copolymer thereof.

Examples of monomer and copolymer thereof include unsaturated carboxylic acids (for example, acrylic acid, methacrylic acid, itaconic acid, crotonic acid, isocrotonic acid, and maleic acid), and esters, amides and copolymers thereof, and preferably include unsaturated carboxylic acid esters, esters of an unsaturated carboxylic acid and an aliphatic polyhydric alcohol compound, and amides of an unsaturated carboxylic acid and an aliphatic polyvalent amine compound.

In particular, esters of an unsaturated carboxylic acid and an aliphatic polyhydric alcohol compound are capable of imparting a high hydrophobicity in a light exposure region, and are thus preferred in that a pattern having a desired shape is easily formed by alkali development and a highly durable pattern is obtained. The effects are remarkable, in particular, in cases in which the wiring density of metal wirings coated with a solder resist is high or a particularly high resistance is required for the solder resist.

In addition, addition reaction products of unsaturated carboxylic acid ester or amide having a nucleophilic substituent group such as a hydroxyl group, an amino group or a mercapto group with a monofunctional or polyfunctional isocyanate or epoxy, or dehydration condensation reaction products of the unsaturated carboxylic acid ester or amide with a monofunctional or polyfunctional carboxylic acid are preferably used.

[0129] Also, preferably used among these compounds are unsaturated carboxylic esters having an electrophilic substituent such as an isocyanate group or an epoxy group, addition-reaction products of amides with monofunctional or multifunctional alcohols, amines or thiols, unsaturated carboxylic esters having an eliminating substituent such as a halogen group and a tosyloxy group, and substitution-reaction products of amides with monofunctional or multifunctional alcohols, amines or thiols. Compounds obtained by replacing the above-described carboxylic acids with unsaturated phosphonic acids, styrene, vinyl ethers etc may be used.

[0130] Unsaturated carboxylic acid esters are preferably methacrylic esters, and examples thereof include tetramethylene glycol dimethacrylate, triethylene glycol dimethacrylate, neopentyl glycol dimethacrylate, trimethylol propane trimethacrylate, trimethylol ethane trimethacrylate, ethylene glycol dimethacrylate, 1,3-butanediol dimethacrylate, hexanediol

dimethacrylate, pentaerythritol dimethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, dipentaerythritol dimethacrylate, dipentaerythritol hexamethacrylate, sorbitol trimethacrylate, sorbitol tetramethacrylate, bis[p-(3-methacryloxy-2-hydroxypropoxy)phenyl]dimethyl methane, and bis[p-(methacryloxyethoxy)phenyl]dimethyl methane, and EO-modified compounds and PO-modified compounds thereof.

[0131] Unsaturated carboxylic acid esters are preferably itaconic acid esters, and examples thereof include ethylene glycol diitaconate, propylene glycol diitaconate, 1,3-butanediol diitaconate, 1,4-butanediol diitaconate, tetramethylene glycol diitaconate, pentaerythritol diitaconate, and sorbitol tetraitaconate. Examples of crotonic acid esters include ethylene glycol dicrotonate, tetramethylene glycol dicrotonate, pentaerythritol dicrotonate, and sorbitol tetradicrotonate. Examples of isocrotonic acid esters include ethylene glycol diisocrotonate, pentaerythritol diisocrotonate and sorbitol tetraisocrotonate. Examples of maleic acid esters include ethylene glycol dimaleate, triethylene glycol dimaleate, pentaerythritol dimaleate, and sorbitol tetramaleate.

[0132] Specific examples of monomers of esters of aliphatic polyhydric alcohol compounds and unsaturated carboxylic acids include (meth)acrylic acid esters such as ethylene glycol diacrylate, triethylene glycol diacrylate, 1,3-butanediol diacrylate, tetramethylene glycol acrylate, propylene glycol diacrylate, neopentyl glycol diacrylate, trimethylol propane triacrylate, trimethylol propane tri(acryloyloxypropyl)ether, trimethylol ethane triacrylate, hexanediol diacrylate, 1,4-cyclohexanediol diacrylate, tetraethylene glycol diacrylate, tricyclodecane dimethanol diacrylate, tricyclodecane dimethanol dimethacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol diacrylate, dipentaerythritol hexaacrylate, sorbitol triacrylate, sorbitol tetraacrylate, sorbitol pentaacrylate, sorbitol hexaacrylate, tri(acryloyloxyethyl) isocyanurate, and polyester acrylate oligomers. In addition, EO-modified compounds, or PO-modified compounds of these compounds may be used.

[0133] Other examples of preferable esters include aliphatic alcohol esters as described in JP-B No. 51-47334 and JP-A No. 57-196231, esters having an aromatic skeleton as described in JP-A No. 59-5240, JP-A No. 59-5241 and JP-A No. 2-226149, and esters having an amino group as described in JP-A No. 1-165613. Also, a mixture of the ester monomers may be used.

[0134] Examples of monomers of the amides formed by reaction between aliphatic polyvalent amine compounds and unsaturated carboxylic acids include methylene bis-acrylamide, methylene bis-methacrylamide, 1,6-hexamethylene bis-acrylamide, 1,6-hexamethylene bis-methacrylamide, diethylenetriamine trisacrylamide, xylylene

bisacrylamide, and xylylene bismethacrylamide. Preferable examples of other amide-containing monomers include those having a cyclohexylene structure as described in JP-B No. 54-21726.

[0135] Urethane-containing addition-polymerizable compounds produced by addition reaction between isocyanates and hydroxyl groups are also preferable, and examples thereof include a vinyl urethane compound containing two or more polymerizable vinyl groups in a molecule, which is prepared by adding a vinyl monomer containing a hydroxyl group shown in Formula (E) below to a polyisocyanate compound having two or more isocyanate groups in a molecule, as described in JP-B No. 48-41708.

[0136] $\text{CH}_2=\text{C}(\text{R}^4)\text{COOCH}_2\text{CH}(\text{R}^5)\text{OH}$ Formula (E)

In Formula (E), R^4 and R^5 each independently represent H or CH_3 .

[0137] Further, urethane acrylates such as those described in JP-A No. 51-37193, and JP-B Nos. 2-32293 and 2-16765, and urethane compounds having an ethylene oxide skeleton described in JP-B Nos. 58-49860, 56-17654, 62-39417, and 62-39418 are also preferable. Furthermore, when addition polymerizable compounds having an amino structure or a sulfide structure in the molecule, which is described in JP-A Nos. 63-277653, 63-260909, and 1-105238 is used, a photo-polymerizable composition having an extremely excellent photosensitization speed is obtained.

[0138] Other examples include multifunctional acrylates and methacrylates such as polyester acrylates and epoxy acrylates obtained by reacting an epoxy resin with (meth)acrylic acid, as described in JP-A No. 48-64183, JP-B No. 49-43191 and JP-B 52-30490. Other examples include specific unsaturated compounds described in JP-B No. 46-43946, JP-B No. 1-40337 and JP-B No. 1-40336 and vinyl phosphonic acid compounds as described in JP-A No. 2-25493. In some cases, a structure containing a perfluoroalkyl group as described in JP-A No. 61-22048 is preferably used. Furthermore, photocurable monomers and oligomers described in the Journal of Adhesive Society of Japan, vol. 20, No. 7, pp. 300-308 (1984) may also be used.

[0139] When a radical polymerizable compound is to be added in the present invention, from the viewpoint of curing sensitivity, use of a multifunctional polymerizable compound containing two or more ethylenically unsaturated bonds is preferred, and use of a multifunctional polymerizable compound containing three or more ethylenically unsaturated bonds is more preferred. In particular, a multifunctional polymerizable compound containing two or more (meth)acrylic acid ester structures are preferred, a multifunctional polymerizable compound containing three or more (meth)acrylic acid ester structures is more preferred, and a multifunctional polymerizable compound containing four or more

(meth)acrylic acid ester structures is most preferred.

From the viewpoints of curing sensitivity and developability of an unexposed region, a compound containing an EO-modified compound is preferably used. From the viewpoints of curing sensitivity and strength of an exposed region, a compound containing a urethane bond is preferably used. From the viewpoint of developability during pattern formation, a compound containing an acidic group is preferred.

[0140] From these viewpoints, examples of preferred polymerizable compounds used in the present invention include bisphenol A diacrylate, EO-modified bisphenol A diacrylate, trimethylolpropane triacrylate, trimethylolpropane tri(acryloyloxypropyl)ether, trimethylolethane triacrylate, tetraethylene glycol diacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, sorbitol triacrylate, sorbitol tetraacrylate, sorbitol pentaacrylate, sorbitol hexaacrylate, tri(acryloyloxyethyl) isocyanurate, EO-modified pentaerythritol tetraacrylate, and EO-modified dipentaerythritol hexaacrylate. In addition, commercially available polymerizable compound products include urethane oligomers UAS-10, UAB-140 (all trade names, manufactured by Sanyo Kokusaku Pulp Corp.), DPHA-40 H (trade name, manufactured by Nippon Kayaku Co., Ltd.), UA-306H, UA-306T, UA-306I, AH-600, T-600, AI-600 (all trade names, manufactured by Kyoeisha Chemical Co., Ltd.).

[0141] Of these, EO-modified bisphenol A diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, tri(acryloyloxyethyl) isocyanurate, EO-modified pentaerythritol tetraacrylate, and EO-modified dipentaerythritol hexaacrylate are preferred. More preferred commercially available products are DPHA-40H (trade name, manufactured by Nippon Kayaku Co., Ltd.), UA-306H, UA-306T, UA-306 I, AH-600, T-600, AI-600 (all trade names, manufactured by Kyoeisha Chemical Co., Ltd.).

Ethylenically unsaturated compounds having an acidic group are also preferred, and examples of commercially available products thereof include TO-756, which is a carboxyl group-containing trifunctional acrylate, and TO-1382, which is a carboxyl group-containing pentafunctional acrylate (all trade names, manufactured by Toagosei Co., Ltd.).

[0142] Other examples include highly heat-resistant polymerizable compounds such as benzocyclobutene (BCB), bis(allyl)nadimide (BANI), benzoxazine, melamine and analogs thereof.

[0143] The polymerizable compound may be used in combination of two or more types thereof.

The content of polymerizable compound (i.e., total content) is preferably from 3% by mass to 80% by mass, more preferably, and from 5% by mass to 80% by mass, with respect to the total solid mass of the light-shielding composition of the present invention.

When the polymerizable compound is a polymer, the polymerizable compound may be the same as the alkali-soluble binder described in detail below (that is, the polymerizable compound and the alkali-soluble binder may be the same component). In this case, the content of polymerizable compound is preferably from 3% by mass to 80% by mass, and more preferably from 5% by mass to 60% by mass, with respect to the total solid mass of the light-shielding composition of the present invention.

[0144] *(E) Photopolymerization initiator*

The light-shielding composition of the present invention preferably contains an (E) photopolymerization initiator.

In the present invention, any photopolymerization initiator is not particularly limited so long as it is capable of initiating polymerization of the polymerizable compound in response to at least one of light and heat, and may be appropriately selected depending on a purpose. The photopolymerization initiator is preferably a photopolymerizable compound. When polymerization is to be initiated using light, a photopolymerization initiator having photo-sensitivity to light from an ultraviolet region to a visible light region is preferred.

When polymerization is to be initiated using heat, an initiator that degrades at 150°C to 250°C is preferred.

[0145] The photopolymerization initiator that can be used for the present invention is preferably a compound having at least an aromatic group, and examples thereof include acyl phosphine compounds, acetophenone compounds, α -amino ketone compounds, benzophenone compounds, benzoin ether compounds, ketal derivative compounds, thioxanthone compounds, oxime compounds, hexaarylbiimidazole compounds, trihalomethyl compounds, azo compounds, organic peroxides, onium salt compounds such as diazonium compounds, iodonium compounds, sulfonium compounds, or azinium compounds, metallocene compounds, organic boron salt compounds, and disulfone compounds.

From the viewpoint of sensitivity, oxime compounds, acetophenone compounds, α -amino ketone compounds, trihalomethyl compounds, hexaaryl biimidazole compounds and thiol compounds are preferred.

Hereinafter, examples of preferable photopolymerization initiators in the present invention will be described, but the present invention is not limited thereto.

[0146] Specific examples of the acetophenone compounds include 2,2-diethoxyacetophenone, p-dimethylaminoacetophenone, 2-hydroxy-2-methyl-1-phenyl-

propan-1-one, p-dimethylaminoacetophenone, 4'-isopropyl-2-hydroxy-2-methylpropiophenone, 1-hydroxy-cyclohexyl-phenyl-ketone, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1, 2-tolyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1, 2-methyl-1-[4-(methylthio) phenyl]-2-morpholinopropanone-1, 2-methyl-1-(4-methylthio phenyl)-2-morpholinopropan-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1, 2-(dimethylamino)-2-[(4-methylphenyl) methyl]-1-[4-(4-morpholinyl)phenyl]-1-butanone, and 2-methyl-1-(4-methylthio phenyl)-2-morpholinopropan-1-one.

[0147] More suitable trihalomethyl compounds are s-triazine derivatives in which at least one mono-, di-, or tri-halogen substituted methyl group is linked to a s-triazine ring, and specific examples thereof include 2,4,6-tris(monochloromethyl)-s-triazine, 2,4,6-tris(dichloromethyl)-s-triazine, 2,4,6-tris(trichloromethyl)-s-triazine, 2-methyl-4,6-bis(trichloromethyl)-s-triazine, 2-n-propyl-4,6-bis(trichloromethyl)-s-triazine, 2-(α,α,β -trichloroethyl)-4,6-bis(trichloromethyl)-s-triazine, 2-phenyl-4,6-bis(trichloromethyl)-s-triazine, 2-(p-methoxyphenyl)-4,6-bis(trichloromethyl)-s-triazine, 2-(3,4-epoxyphenyl)-4,6-bis(trichloromethyl)-s-triazine, 2-(p-chlorophenyl)-4,6-bis(trichloromethyl)-s-triazine, 2-[1-(p-methoxyphenyl)-2,4-butadienyl]-4,6-bis(trichloromethyl)-s-triazine, 2-styryl-4,6-bis(trichloromethyl)-s-triazine, 2-(p-methoxystyryl)-4,6-bis(trichloromethyl)-s-triazine, 2-(p-i-propyloxystyryl)-4,6-bis(trichloromethyl)-s-triazine, 2-(p-tolyl)-4,6-bis(trichloromethyl)-s-triazine, 2-phenylthio-4,6-bis(trichloromethyl)-s-triazine, 2-benzylthio-4,6-bis(trichloromethyl)-s-triazine, 2,4,6-tris(dibromomethyl)-s-triazine, 2,4,6-tris(tribromomethyl)-s-triazine, 2-methyl-4,6-bis(tribromomethyl)-s-triazine, and 2-methoxy-4,6-bis(tribromomethyl)-s-triazine.

[0148] Examples of hexaaryl biimidazole compounds include a variety of compounds disclosed in JP-A No. 6-29285, and US Patent Nos. 3,479,185, 4,311,783, and 4,622,286 and the like, and specific examples thereof include 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetraphenylbiimidazole, 2,2'-bis(o-bromophenyl)-4,4',5,5'-tetraphenylbiimidazole, 2,2'-bis(o,p-dichlorophenyl)-4,4',5,5'-tetraphenylbiimidazole, 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetra(m-methoxyphenyl) biimidazole, 2,2'-bis(o,o'-dichlorophenyl)-4,4',5,5'-tetraphenylbiimidazole, 2,2'-bis(o-nitrophenyl)-4,4',5,5'-tetraphenylbiimidazole, 2,2'-bis(o-methylphenyl)-4,4',5,5'-tetraphenylbiimidazole, and 2,2'-bis(o-trifluorophenyl)-4,4',5,5'-tetraphenylbiimidazole.

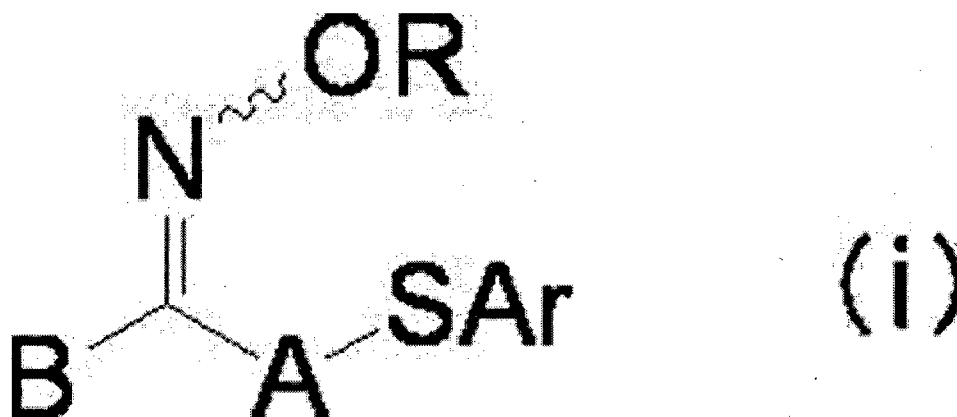
[0149] Examples of oxime compounds include compounds described in J. C. S. Perkin II (1979) pages 1653 to 1660, J. C. S. Perkin II (1979) pages 156 to 162, Journal of Photopolymer Science and Technology (1995) pages 202 to 232, and JP-A No. 2000-66385, and compounds described in JP-A No. 2000-80068, and Japanese National Phase Publication

No. 2004-534797. Commercially available products thereof such as IRGACURE OXE 01 (1,2-octanedione, 1-[4-(phenylthio)-, 2-(O-benzoyloxime)]), IRGACURE OXE 02 (ethanone, 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazole 3-yl]-, 1-(O-acetyloxime)), 2-(acetyloxyiminomethyl) thioxanthen-9-one (all trade names, manufactured by BASF Corporation, Japan) are also preferably used.

Cyclic oxime compounds disclosed in JP-A No. 2007-231000 and JP-A No. 2007-322744 are also preferred. An oxime compound having a specific substituent as disclosed in JP-A No. 2007-269779, or an oxime compound having a thioaryl group disclosed in JP-A No. 2009-191061 is also most preferred.

Specifically, oxime compounds are preferably compounds represented by the following Formula (i). In addition, the oxime compound may be an oxime compound of (E) form, in which the N-O bond of the oxime is in the (E) form, or an oxime compound of (Z) form, in which the N-O bond of the oxime is in the (Z) form, or may be a mixture of the (E) form and the (Z) form.

[0150]



[0151] In Formula (i), R and B each independently represent a monovalent substituent, A represents a divalent organic group, and Ar represents an aryl group.

The monovalent substituent represented by R in Formula (i) is preferably a monovalent non-metal atomic group. Examples of the monovalent non-metal atomic group include an alkyl group, an aryl group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, a heterocyclic group, an alkyl thiocarbonyl group, and an aryl thiocarbonyl group. In addition, these groups may each have one or more substituents. In addition, the substituent(s) may be further substituted by another substituent.

Examples of the substituents include a halogen atom, an aryloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, an acyloxy group, an acyl group, an alkyl group, and an aryl group.

[0152] The alkyl group which may have a substituent is preferably an alkyl group having 1 to 30 carbon atoms. Specific examples thereof include a methyl group, an ethyl group, a propyl group, a butyl group, a hexyl group, an octyl group, a decyl group, a dodecyl group, an octadecyl group, an isopropyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, a 1-ethylpentyl group, a cyclopentyl group, a cyclohexyl group, a trifluoromethyl group, a 2-ethylhexyl group, a phenacyl group, a 1-naphthoylmethyl group, a 2-naphthoylmethyl group, a 4-methylsulfanyphenacyl group, a 4-phenylsulfanyphenacyl group, a 4-dimethylaminophenacyl group, a 4-cyanophenacyl group, a 4-methylphenacyl group, a 2-methylphenacyl group, a 3-fluorophenacyl group, a 3-trifluoromethylphenacyl group, and a 3-nitrophenacyl group.

[0153] The aryl group which may have a substituent is preferably an aryl group having 6 to 30 carbon atoms. Specific examples thereof include a phenyl group, a biphenyl group, a 1-naphthyl group, a 2-naphthyl group, a 9-anthryl group, a 9-phenanthryl group, a 1-pyrenyl group, a 5-naphthacenyl group, a 1-indenyl group, a 2-azulenyl group, a 9-fluorenyl group, a terphenyl group, a quaterphenyl group, an o-tolyl group, a m-tolyl group, a p-tolyl group, a xylyl group, an o-cumenyl group, a m-cumenyl group, p-cumenyl group, a mesityl group, a pentalenyl group, a binaphthalenyl group, a ternaphthalenyl group, a quaternaphthalenyl group, a heptalenyl group, a biphenylenyl group, an indacenyl group, a fluoranthenyl group, an acenaphthylenyl group, an aceanthrylenyl group, a phenalenyl group, a fluorenyl group, an anthryl group, a bianthracenyl group, a teranthracenyl group, a quateranthracenyl group, an anthraquinolyl group, a phenanthryl group, a triphenylenyl group, a pyrenyl group, a chrysenyl group, a naphthacenyl group, a pleiadenyl group, a picenyl group, a perylenyl group, a pentaphenyl group, a pentacenyl group, a tetraphenylenyl group, a hexaphenyl group, a hexacenyl group, a rubicenyl group, a coronenyl group, a trinaphthylenyl group, a heptaphenyl group, a heptacenyl group, a pyranthrenyl group, and an ovalenyl group.

[0154] The acyl group which may have a substituent is preferably an acyl group having 2 to 20 carbon atoms. Specific examples thereof include an acetyl group, a propanoyl group, a butanoyl group, a trifluoroacetyl group, a pentanoyl group, a benzoyl group, a 1-naphthoyl group, a 2-naphthoyl group, a 4-methylsulfanylbzoyl group, a 4-phenylsulfanylbzoyl group, 4-dimethylaminobenzoyl group, a 4-diethylaminobenzoyl group, a 2-chlorobenzoyl group, a 2-methylbenzoyl group, a 2-methoxybenzoyl group, a 2-butoxybenzoyl group, a 3-chlorobenzoyl group, a 3-trifluoromethylbenzoyl group, a 3-cyanobenzoyl group, a 3-nitrobenzoyl group, a 4-fluorobenzoyl group, a 4-cyanobenzoyl group, and a 4-methoxybenzoyl group.

[0155] The alkoxycarbonyl group which may have a substituent is preferably an

alkoxycarbonyl group having 2 to 20 carbon atoms. Specific examples thereof include a methoxycarbonyl group, an ethoxycarbonyl group, a propoxycarbonyl group, a butoxycarbonyl group, a hexyloxycarbonyl group, an octyloxycarbonyl group, a decyloxycarbonyl group, an octadecyloxycarbonyl group, and a trifluoromethyloxycarbonyl group.

[0156] Specific examples of the aryloxycarbonyl group, which may have a substituent, include a phenoxycarbonyl group, a 1-naphthyloxycarbonyl group, a 2-naphthyloxycarbonyl group, a 4-methylsulfanylphenyloxycarbonyl group, a 4-phenylsulfanylphenyloxycarbonyl group, a 4-dimethylaminophenyloxycarbonyl group, a 4-diethylaminophenyloxycarbonyl group, a 2-chlorophenyloxycarbonyl group, a 2-methylphenyloxycarbonyl group, a 2-methoxyphenyloxycarbonyl group, a 2-butoxyphenyloxycarbonyl group, a 3-chlorophenyloxycarbonyl group, a 3-trifluoromethylphenyloxycarbonyl group, a 3-cyanophenyloxycarbonyl group, a 3-nitrophenyloxycarbonyl group, a 4-fluorophenyloxycarbonyl group, a 4-cyanophenyloxycarbonyl group, and a 4-methoxyphenyloxycarbonyl group.

[0157] The heterocyclic group which may have a substituent is preferably an aromatic or aliphatic heterocycle containing a nitrogen atom, an oxygen atom, a sulfur atom, or a phosphorus atom.

Specific examples thereof include a thienyl group, a benzo[b]thienyl group, a naphtho[2,3-b]thienyl group, a thianthrenyl group, a furyl group, a pyranyl group, an isobenzofuranyl group, a chromenyl group, a xanthenyl group, a phenoxanthiynyl group, a 2H-pyrrolyl group, a pyrrolyl group, an imidazolyl group, a pyrazolyl group, a pyridyl group, a pyrazinyl group, a pyrimidinyl group, a pyridazinyl group, an indolizinyl group, an isoindolyl group, a 3H-indolyl group, an indolyl group, a 1H-indazolyl group, a purinyl group, a 4H-quinolizinyl group, an isoquinolyl group, a quinolyl group, a phthalazinyl group, a naphthyridinyl group, a quinoxalinyl group, a quinazolinyl group, a cinnolinyl group, a pteridinyl group, a 4aH-carbazolyl group, a carbazolyl group, a β -carbolinyl group, a phenanthridinyl group, an acridinyl group, a perimidinyl group, a phenanthrolinyl group, a phenazinyl group, a phenarsazinyl group, an isothiazolyl group, a phenothiazinyl group, an isoxazolyl group, a furazanyl group, a phenoxazinyl group, an isochromanyl group, a chromanyl group, a pyrrolidinyl group, a pyrrolinyl group, an imidazolidinyl group, an imidazolinyll group, a pyrazolidinyl group, a pyrazolinyl group, a piperidyl group, a piperazinyl group, an indolinyl group, an isoindolinyl group, a quinuclidinyl group, a morpholinyl group, and a thioxanthryl group.

[0158] Specific examples of the alkylthiocarbonyl group, which may have a substituent,

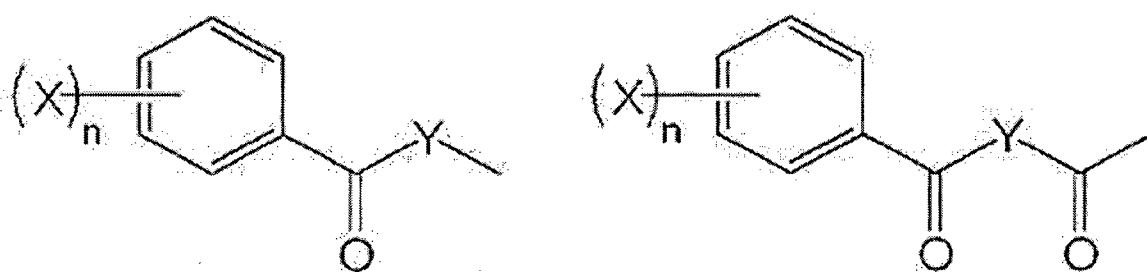
include a methylthiocarbonyl group, a propylthiocarbonyl group, a butylthiocarbonyl group, a hexylthiocarbonyl group, an octylthiocarbonyl group, a decylthiocarbonyl group, an octadecylthiocarbonyl group, and a trifluoromethylthiocarbonyl group.

[0159] Specific examples of the alkylthiocarbonyl group, which may have a substituent, include a 1-naphthylthiocarbonyl group, a 2-naphthylthiocarbonyl group, a 4-methylsulfanylphenylthiocarbonyl group, a 4-phenylsulfanylphenylthiocarbonyl group, a 4-dimethylaminophenylthiocarbonyl group, a 4-diethylaminophenylthiocarbonyl group, a 2-chlorophenylthiocarbonyl group, a 2-methylphenylthiocarbonyl group, a 2-methoxyphenylthiocarbonyl group, a 2-butoxyphenylthiocarbonyl group, a 3-chlorophenylthiocarbonyl group, a 3-trifluoromethylphenylthiocarbonyl group, a 3-cyanophenylthiocarbonyl group, a 3-nitrophenylthiocarbonyl group, a 4-fluorophenylthiocarbonyl group, a 4-cyanophenylthiocarbonyl group, and a 4-methoxyphenylthiocarbonyl group.

[0160] The monovalent substituent represented by B in Formula (i) represents an aryl group, a heterocyclic group, an arylcarbonyl group, or a heterocyclic carbonyl group. These groups may have one or more substituents. As the substituent, the above-described substituents may be exemplified. Further, the substituent may further be substituted by another substituent.

[0161] In particular, the following structures are particularly preferable. In the following structures, Y, X, and n have the same definitions as Y, X, and n in Formula (ii) described below, respectively, and preferable examples thereof are also the same.

[0162]



[0163] Examples of the divalent organic group represented by A in Formula (i) include an alkylene group, a cyclohexylene group, and an alkynylene group each having 1 to 12 carbon atoms. These groups may have one or more substituents. As the substituent, the above-described substituents may be exemplified. Further, the substituent may further be substituted by another substituent.

In particular, from the viewpoints of enhancing the sensitivity and suppressing

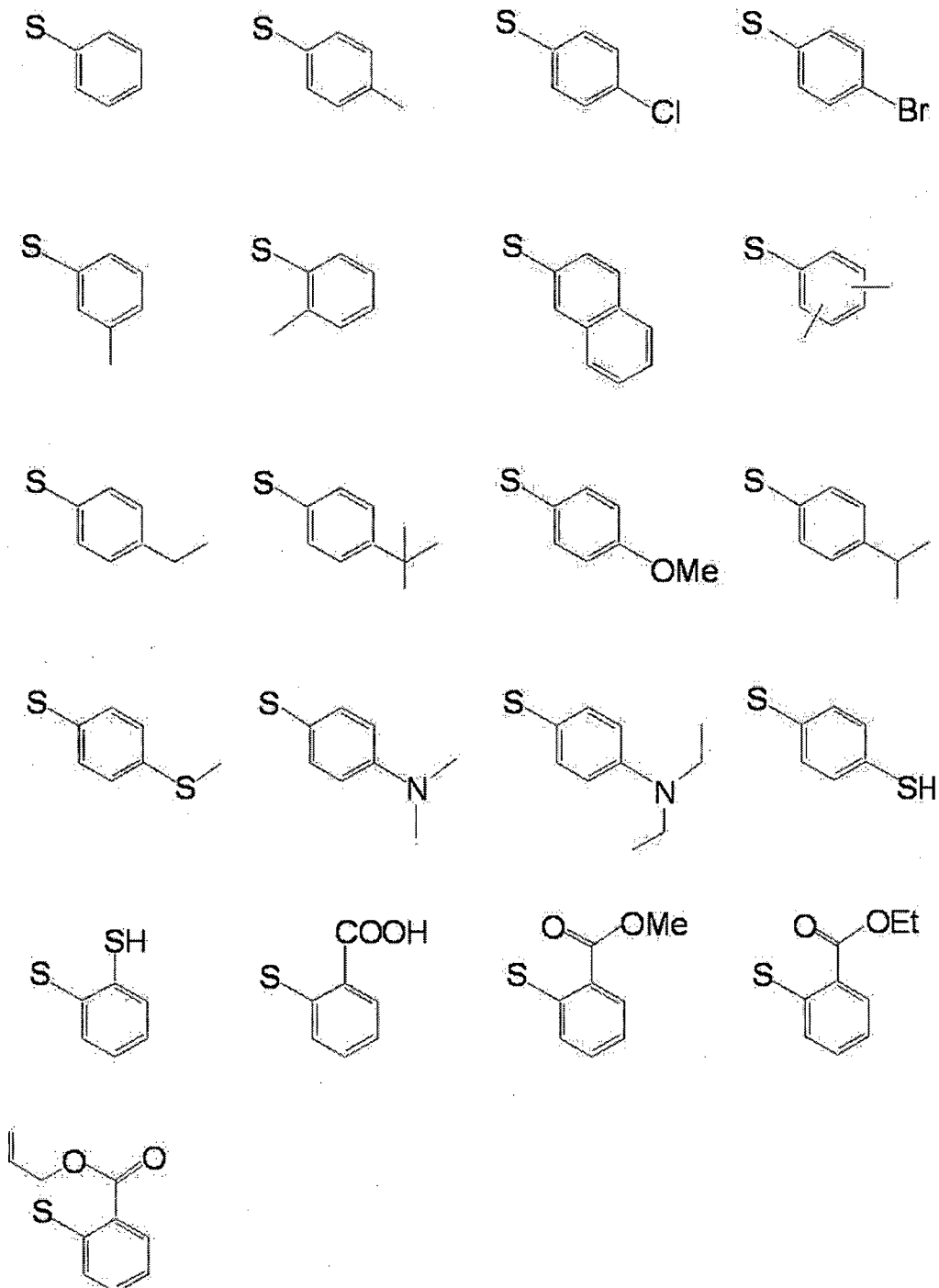
coloration due to thermal aging, A in Formula (i) preferably represents an unsubstituted alkylene group, an alkylene group substituted by an alkyl group (such as a methyl group, an ethyl group, a tert-butyl group, or a dodecyl group), an alkylene group substituted by an alkenyl group (such as a vinyl group or an allyl group), and an alkylene group substituted by an aryl group (such as a phenyl group, a p-tolyl group, a xylyl group, a cumenyl group, a naphthyl group, an anthryl group, a phenanthryl group, or a styryl group).

[0164] The aryl group represented by Ar in Formula (i) is preferably an aryl group having 6 to 30 carbon atoms, and may have a substituent. Examples of the substituent include those which are the same as the substituents introduced into the substituted aryl groups which are described above as specific examples of the aryl group which may have a substituent.

In particular, from the viewpoints of enhancing the sensitivity and suppressing of the coloration due to thermal aging, Ar in Formula (i) is preferably a substituted or unsubstituted phenyl group.

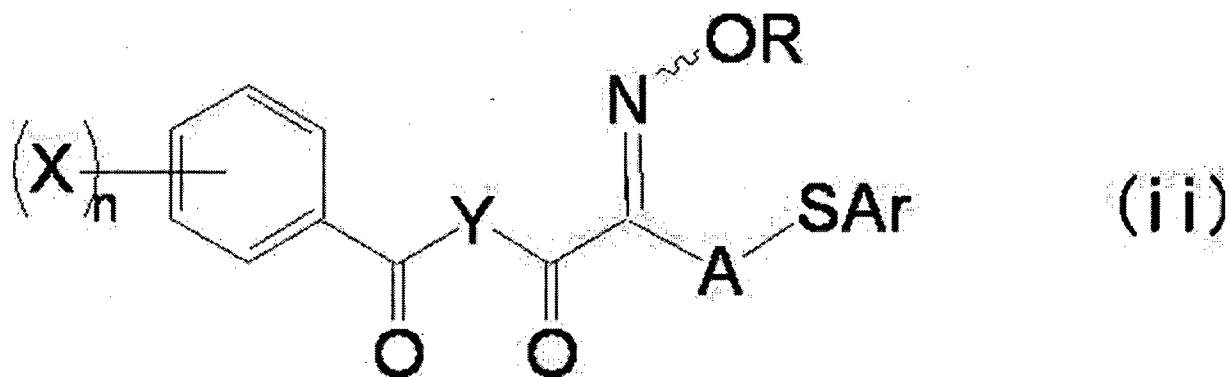
[0165] In Formula (i), the structure of "SAr" that is formed by Ar and the adjacent S is preferably the structure shown below, from the viewpoint of sensitivity. In this case, "Me" represents a methyl group, and "Et" represents an ethyl group.

[0166]



[0167] It is preferable that the oxime compound is a compound represented by the following Formula (ii).

[0168]



[0169] In Formula (ii), R and X each independently represent a monovalent substituent, A and Y each independently represent a divalent organic group, Ar represents an aryl group, and n represents an integer of 0 to 5.

R, A, and Ar in Formula (ii) have the same definitions as R, A, and Ar in Formula (i) described above, respectively, and preferable ranges (including preferable examples) thereof are also the same.

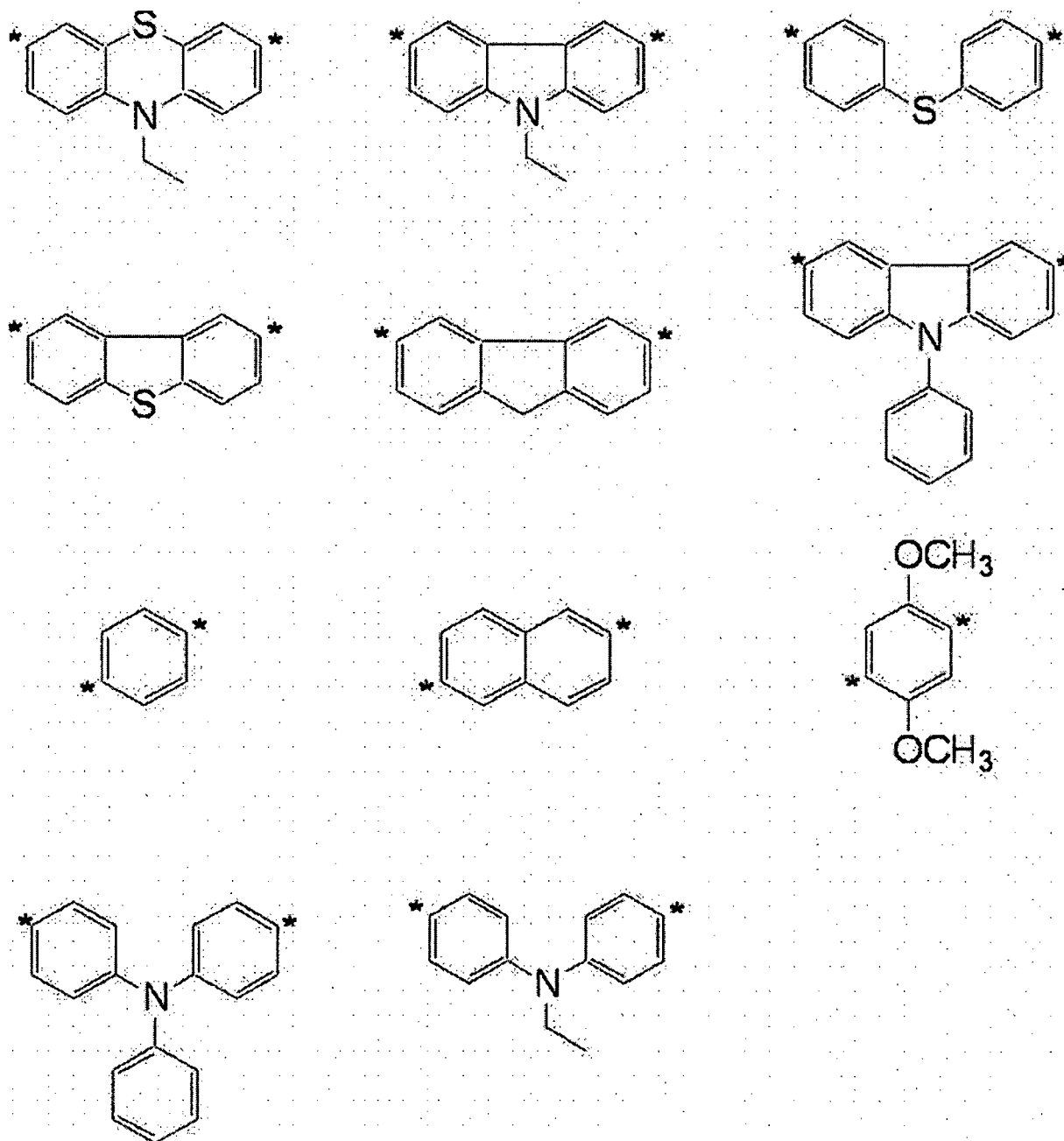
[0170] Specific examples of the monovalent substituent represented by X include an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an acyloxy group, an acyl group, an alkoxycarbonyl group, an amino group, a heterocyclic group, and a halogen atom. These groups may each have one or more substituents. Examples of the substituent may include the substituents described above. The substituents may further be substituted by another substituent.

[0171] Among them, X preferably represents an alkyl group, from the viewpoints of solvent solubility and improvement in absorption efficiency in a long wavelength region.

Furthermore, n in Formula (ii) represents an integer of 0 to 5, and preferably represents an integer of 0 to 2.

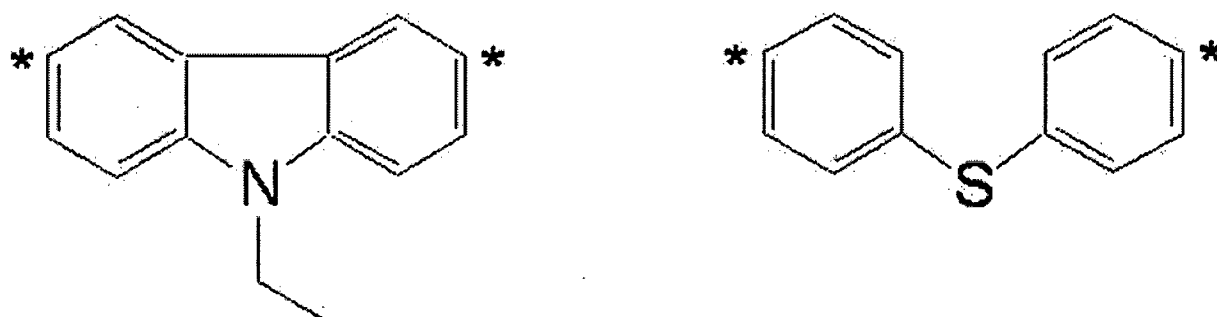
[0172] Examples of the divalent organic group represented by Y in Formula (ii) include the following structures. In the groups described below, "*" denotes a bonding position to a carbon atom adjacent to Y in Formula (ii) above.

[0173]



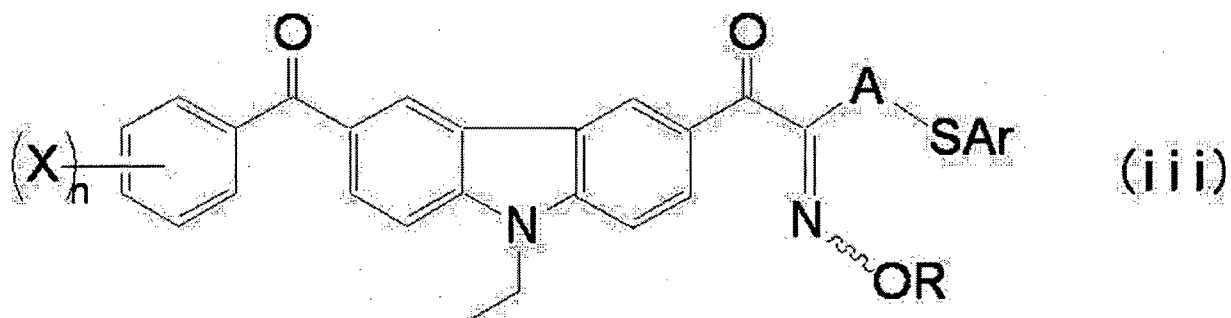
[0174] Among the above structures, the structures shown below are preferable from the viewpoint of enhancing the sensitivity.

[0175]



[0176] Further, the oxime compound is preferably a compound represented by the following Formula (iii).

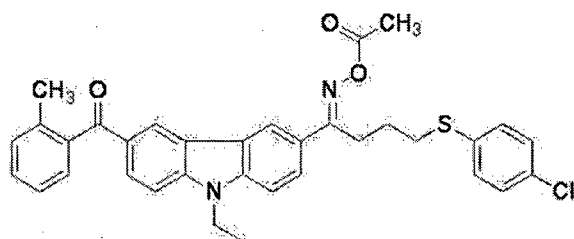
[0177]



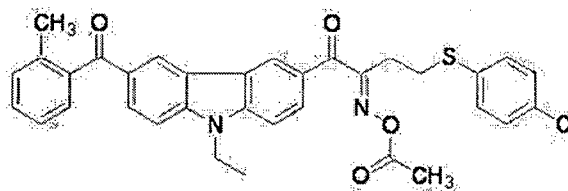
[0178] R, X, A, Ar, and n in Formula (iii) have the same definitions as R, X, A, Ar, and n in Formula (ii) described above, respectively, and preferable ranges (including preferable examples) thereof are also the same.

[0179] Specific examples (C-4) to (C-13) of the oxime compound which is preferably used are shown below, but it should be construed that the present invention is not limited thereto.

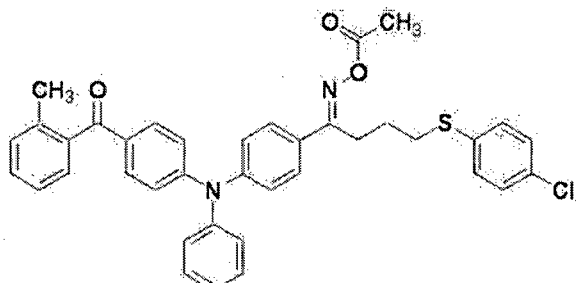
[0180]



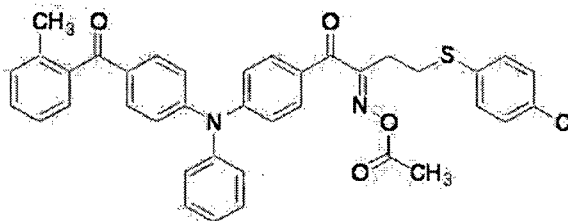
(C-4)



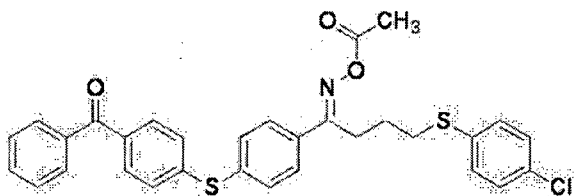
(C-5)



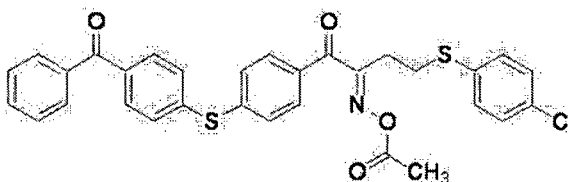
(C-6)



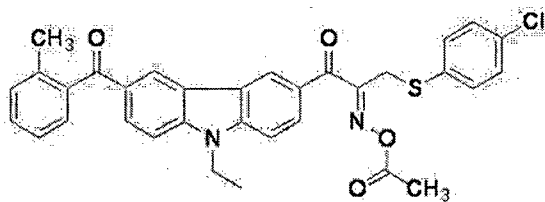
(C-7)



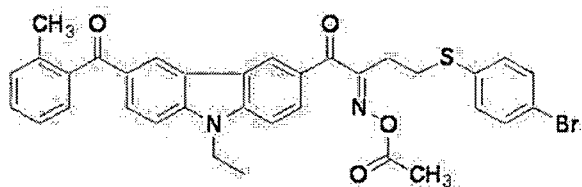
(C-8)



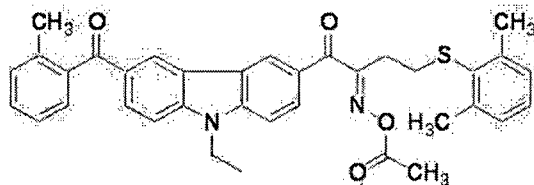
(C-9)



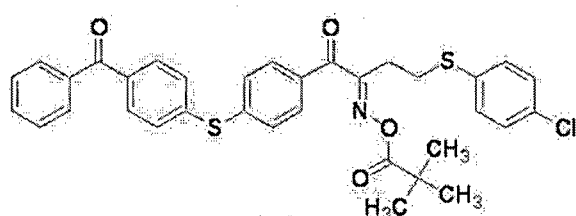
(C-10)



(C-11)



(C-12)



(C-13)

[0181] The oxime compound preferably has a maximum absorption wavelength in a wavelength region of from 350 nm to 500 nm, more preferably has an absorption wavelength in a wavelength region of from 360 nm to 480 nm, and particularly preferably has a high absorbance at 365 nm and 455 nm.

[0182] From the viewpoint of sensitivity, the oxime compound preferably has a molar absorption coefficient at 365 nm or 405 nm of from 3,000 to 300,000, more preferably from 5,000 to 300,000, and particularly preferably from 10,000 to 200,000.

The molar absorption coefficient of a compound may be measured by a known method. Specifically, it is preferable to measure a molar absorption coefficient using, for example, an ultraviolet-visible spectrometer (trade name: CARRY-5 SPECTROPHOTOMETER, manufactured by Varian), at a concentration of 0.01 g/L using an ethyl acetate solvent.

[0183] The photopolymerization initiator is more preferably a compound selected from the group consisting of oxime compounds, acetophenone compounds, and acyl phosphine compounds. Specific examples thereof include aminoacetophenone initiators disclosed in JP-A No. 10-291969, and in particular, acyl phosphine oxide initiators disclosed in Japanese Patent No. 4225898 and conventional oxime initiators, and in particular, oxime initiators, such as compounds disclosed in JP-A No. 2001-233842.

Examples of acetophenone initiators include commercially available products, IRGACURE-907, IRGACURE-369 and IRGACURE-379 (all trade names, manufactured by BASF Corporation, Japan.). Examples of acyl phosphine initiators include acyl phosphine initiators including commercially available products such as IRGACURE-819 or DAROCUR-TPO (all trade names, manufactured by BASF Corporation, Japan).

[0184] The photopolymerization initiator may be used alone or in combination of two or more types thereof.

The content of photopolymerization initiator in the light-shielding composition of the present invention is preferably 0.01% by mass to 30% by mass, more preferably 0.1% by mass to 20% by mass, and particularly preferably 0.1% by mass to 15% by mass, with respect to the total solid mass of the composition.

[0185] Hereinafter, other components preferably contained in the light-shielding composition of the present invention will be described.

Sensitizing agent

The light-shielding composition of the present invention preferably contains a sensitizing agent.

When the sensitizing agent is used in combination with the photopolymerization initiator, a light-shielding composition with high adhesivity is obtained even when illuminance during radiation curing is relatively low.

[0186] Examples of the sensitizing agent include amines compounds as disclosed in M. R. Sander *et. al*, "Journal of Polymer Society", Vol. 10, p 3173 (1972), JP-B No. 44-20189, JP-A

No. 51-82102, JP-A No. 52-134692, JP-A No. 59-138205, JP-A No. 60-84305, JP-A No. 62-18537, JP-A No. 64-33104, and Research Disclosure No. 33825. Specific examples thereof include triethanolamine, p-dimethylaminoethyl benzoate ester, p-formyl dimethylaniline, and p-methyl thioldimethyl.

[0187] Other examples of the sensitizing agent include thiols and sulfides, for example, thiol compounds disclosed in JP-A No. 53-702, JP-B No. 55-500806 and JP-A No. 5-142772, disulfide compounds disclosed in JP-A No. 56-75643 and the like. Specific examples thereof include 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-mercaptobenzoimidazole, N-phenylmercaptobenzoimidazole, 2-mercapto-4(3H)-quinazoline, and β -mercapto naphthalene.

[0188] Other examples thereof include amino acid compounds (for example, N-phenylglycine, and the like), organic metal compounds (for example, tributyl acetate and the like) disclosed in JP-B No. 48-42965, hydrogen donors disclosed in JP-B No. 55-34414, sulfur compounds (for example, trithiane and the like) disclosed in JP-A No. 6-308727 and the like.

[0189] The content of sensitizing agent is preferably 0.1% to 30% by mass, more preferably 1% to 25%, and most preferably 0.5% to 20%, with respect to the total solid of the light-shielding composition, from the viewpoints of improvement in curing rate by balance between polymer growth rate and chain transfer.

[0190] *Alkali-soluble binder*

The light-shielding composition of the present invention preferably contains an alkali-soluble binder.

In a case in which the light-shielding composition contains an alkali-soluble binder, an unexposed region may be removed by an alkaline developing solution when light exposure is performed to form a pattern on a film formed from the light-shielding composition, and an excellent pattern is thus formed by alkaline development.

[0191] The alkali-soluble binder is not particularly limited as long as it is alkali-soluble, and may be appropriately selected depending on purpose. Examples thereof include (meth)acrylic resins, urethane resins, polyvinyl alcohols, polyvinyl butyrals, polyvinylformals, polyamides, and polyesters. Among these, (meth)acrylic resins or urethane resins are preferred.

In particular, the alkali-soluble binder is more preferably a urethane resin from the viewpoints of further improvement in thermal cycle test resistance (TCT resistance).

The alkali-soluble binder preferably has an acidic group.

Examples of the acidic group include a carboxylic acid group, a sulfonic acid group,

a phosphonic acid group, a phosphate group, and a sulfone amide group. The acidic group is preferably a carboxylic acid group from the viewpoint of availability of materials.

[0192] The alkali-soluble binder having an acidic group is not particularly limited and is preferably a polymer obtained using a polymerizable compound having an acidic group as a monomer component. From the viewpoint of controllability of acid value, a copolymer obtained by copolymerizing a polymerizable compound having an acidic group and a polymerizable compound having no acidic group is more preferred.

[0193] The polymerizable compound having an acidic group is not particularly limited and may be appropriately selected depending on the purpose. Examples thereof include acrylic acid, methacrylic acid, itaconic acid, crotonic acid, isocrotonic acid, maleic acid, and p-carboxystyrene. Among these, acrylic acid, methacrylic acid and p-carboxystyrene are preferred. These may be used alone or in combination of two or more types thereof.

[0194] The polymerizable compound having no acidic group is not particularly limited, but preferable examples thereof include (meth)acrylic acid esters (such as alkylesters, arylestes, or aralkyl esters).

The alkyl group of an alkylester moiety in a (meth)acrylic acid ester may be a straight chain or branched alkyl group, and is preferably an alkyl group having 1 to 10 carbon atoms, and more preferably an alkyl group having 1 to 6 carbon atoms.

The aryl group in an arylester moiety in a (meth)acrylic acid ester is preferably an aryl group having 6 to 14 carbon atoms, and more preferably, an aryl group having 6 to 10 carbon atoms.

The aralkyl group in an aralkyl ester moiety of a (meth)acrylic acid ester is preferably an aralkyl group having 7 to 20 carbon atoms, more preferably an aralkyl group having 7 to 12 carbon atoms.

[0195] A molar ratio of a monomer corresponding to the polymerizable compound having an acidic group to a monomer corresponding to the polymerizable compound having no acidic group (i.e., monomer corresponding to the polymerizable compound having an acidic group : monomer corresponding to the polymerizable compound having no acidic group) is generally from 1:99 to 99:1, preferably from 30:70 to 99:1, and more preferably from 50:50 to 99:1.

The content of the acidic group in the alkali-soluble binder is not particularly limited, but is preferably 0.5 meq/g to 4.0 meq/g, and more preferably 1.0 meq/g to 3.0 meq/g. When the content is 0.5 meq/g or higher, alkaline developability is sufficiently obtained and an excellent pattern is obtained. When the content is 4.0 meq/g or less, deterioration in strength of a permanent pattern is surely prevented.

[0196] Preferably, the alkali-soluble binder further contains a crosslinkable group. In this

case, both the curing property of an exposed region and the alkali-developability of an unexposed region are improved, and a pattern having a high durability is obtained (the effects are remarkable, in particular, in cases in which the wiring density of metal wirings coated with a solder resist is high or considerably important resistance is required for the solder resist). The term "crosslinkable group" refers to a group which is capable of crosslinking a binder polymer during polymerization which occurs when the photosensitive layer obtained using the light-shielding composition is subjected to light exposure or heating. Any group may be used without particular limitation so long as it has such function, and examples thereof include functional groups which enable addition polymerization such as an ethylenically unsaturated bond group, an amino group, or an epoxy group. In addition, a functional group which is capable of producing a radical owing to light irradiation may be used, and examples of such a crosslinkable group include a thiol group and a halogen group. Of these, an ethylenically unsaturated bond group is preferred. The ethylenically unsaturated bond group is preferably a styryl group, a (meth)acryloyl group, or an allyl group, and is more preferably a (meth)acryloyl group from the viewpoint of the balance between stability of the crosslinkable group prior to light exposure and strength of a permanent pattern.

[0197] The alkali-soluble binder may be, for example, cured by an addition reaction between the crosslinkable functional group thereof and a free radical (e.g., a polymerization initiation radical or a radical produced during polymerization of a polymerizable compound), directly between polymers or through polymerization chain reactions of the polymerizable compounds, and formation of cross-linkage between polymers. Alternatively, an atom in polymers (for example, a hydrogen atom on a carbon atom adjacent to a functional crosslinkable group) is released by free radicals to produce polymer radicals and the radicals are bonded to each other to produce a cross-linkage between the polymers. As a result, the alkali-soluble binder is cured.

[0198] The content of crosslinkable group in the alkali-soluble binder is not particularly limited, but is preferably 0.5 meq/g to 3.0 meq/g, more preferably 1.0 meq/g to 3.0 meq/g, and particularly preferably 1.5 meq/g to 2.8 meq/g. When the content is 0.5 meq/g or higher, the amount of cured component is sufficient, high sensitivity is obtained, and when the content is 3.0 meq/g or lower, the storage stability of light-shielding composition is improved.

Here, the content (meq/g) may be measured by iodine value titration.

The alkali-soluble binder having a crosslinkable group is described in JP-A No. 2003-262958 in detail, and the compounds described therein may be also used in the present invention.

The alkali-soluble binder containing a crosslinkable group is preferably an alkali-

soluble binder having an acid group and a crosslinkable group, and representative examples thereof include the following compounds:

(1) urethane-modified polymerizable double bond-containing acrylic resin which is obtained, for example, by previously reacting isocyanate groups with OH groups, leaving one unreacted isocyanate group and reacting a compound containing at least one (meth)acryloyl group with an acrylic resin containing a carboxyl group; and

(2) an unsaturated group-containing acrylic resin obtained by reacting an acrylic resin containing a carboxyl group with a compound having both an epoxy group and a polymerizable double bond;

(3) a polymerizable double bond-containing acrylic resin which may be obtained, for example, by reacting an acrylic resin containing an OH group with a dibasic acid anhydride containing a polymerizable double bond.

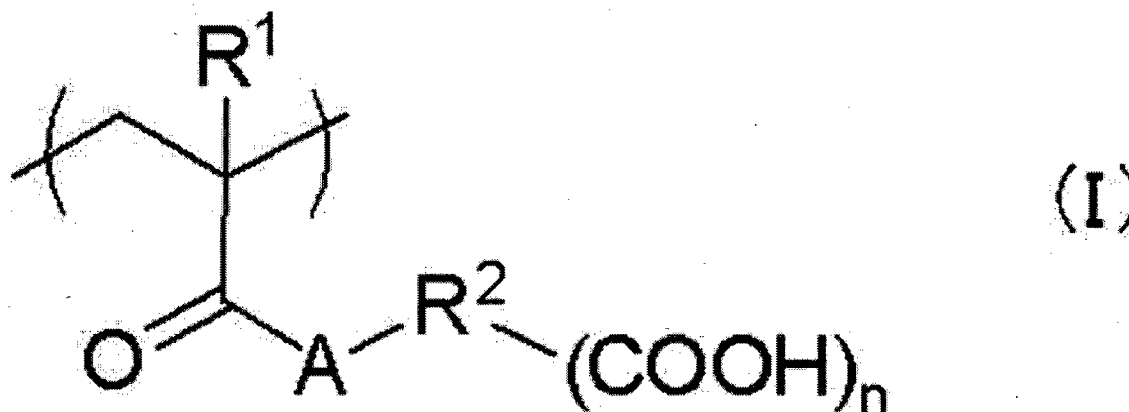
Among these, (1) and (2) resins are particularly preferred.

[0199] Examples of the alkali-soluble binder containing an acid group and a crosslinkable group include polymer compounds that have an acidic group and an ethylenically unsaturated bond at a side chain and has a bisphenol A skeleton and a bisphenol F skeleton, and novolac resins and resol resins that have acidic group and an ethylenically unsaturated bond and the like. These resins may be obtained by the method described in the paragraphs [0008] to [0027] of JP-A No. 11-240930.

[0200] As mentioned above, the alkali-soluble binder is preferably a (meth)acrylic resin or a urethane resin. The "(meth)acrylic resin" is preferably a copolymer that has (meth)acrylic acid, (meth)acrylic acid ester (such as alkyl ester, aryl ester or aralkyl ester), (meth)acrylamide, or a (meth)acrylic acid derivative such as (meth)acrylamide derivative as a polymerizable component. Furthermore, the "urethane resin" is preferably a polymer which is produced by condensation of a compound containing two or more isocyanate groups and a compound containing two or more hydroxyl groups.

[0201] The (meth)acrylic resin is preferably a copolymer having a repeating unit containing an acid group. Examples of the acid group are preferably those as those mentioned above. The repeating unit containing an acidic group is preferably a repeating unit derived from (meth)acrylic acid, or any one of those represented by the following Formula (I).

[0202]



[0203] In Formula (I), R¹ represents a hydrogen atom or a methyl group; R² represents a single bond or an (n+1)-valent linking group; A represents an oxygen atom or -NR³-, in which R³ represents a hydrogen atom or a monovalent hydrocarbon group having 1 to 10 carbon atoms; and n represents an integer of 1 to 5.

[0204] In Formula (I), the linking group represented by R² preferably contains one or more atoms selected from the group consisting of a hydrogen atom, a carbon atom, an oxygen atom, a nitrogen atom, a sulfur atom and a halogen atom. The number of atoms constituting the linking group represented by R² is preferably 1 to 80. Specifically, examples of the linking group represented by R² include an alkylene group and an arylene group, or may have a structure in which two or more of these divalent groups are linked via an amide bond, an ether bond, a urethane bond, a urea bond or an ester bond. R² is preferably a single bond, an alkylene group, or a group formed by linking two or more alkylene groups via an amide bond, an ether bond, a urethane bond, a urea bond or an ester bond.

The number of carbon atoms of the alkylene group is preferably 1 to 5, and more preferably 1 to 3.

The number of carbon atoms of arylene group is preferably 6 to 14, and more preferably 6 to 10.

The alkylene group and the arylene group may each further have a substituent, and examples the substituent include monovalent non-metal atomic groups except a hydrogen atom, such as halogen atoms (-F, -Br, -Cl, -I), a hydroxyl group, a cyano group, an alkoxy group, an aryloxy group, a mercapto group, an alkylthio group, an arylthio group, an alkylcarbonyl group, an arylcarbonyl group, a carboxyl group and a conjugated base group thereof, an alkoxycarbonyl group, an aryloxy carbonyl group, a carbamoyl group, an aryl group, an alkenyl group, and an alkynyl group.

[0205] The number of carbon atoms of the hydrocarbon group represented by R³ is

preferably 1 to 10, more preferably 1 to 5, and even more preferably 1 to 3.

R^3 is most preferably a hydrogen atom or a methyl group.

Furthermore, n is preferably 1 to 3, particularly preferably 1 or 2, and most preferably 1.

[0206] The ratio (mole%) of a repeating unit having an acid group in the total repeating unit components in the (meth)acrylic resin is preferably 10 to 90% from the viewpoint of developability, is more preferably 50 to 85% from the viewpoint from the balance between developability and strength of permanent pattern, and particularly preferably 60 to 80%.

[0207] The (meth)acrylic resin preferably further contains a crosslinkable group as mentioned above, and specific examples and content of the crosslinkable group are the same as mentioned above.

[0208] The (meth)acrylic resin group that can be used in the invention may further contain a polymerization unit of an alkyl (meth)acrylate or aralkyl (meth)acrylate ester, a polymerization unit of (meth)acrylamide or a derivative thereof, a polymerization unit of α -hydroxymethyl acrylate or a polymerization unit of a styrene derivative, in addition to the polymerization unit having an acid group and the polymerization unit having a crosslinkable group as described above. The alkyl group in the alkyl (meth)acrylate ester is preferably an alkyl group having 1 to 5 carbon atoms or an alkyl group having 2 to 8 carbon atoms and having the substituent mentioned above, and is more preferably a methyl group. The aralkyl (meth)acrylate ester includes, for example, benzyl (meth)acrylate. The (meth)acrylamide derivative includes, for example, N-isopropylacrylamide, N-phenylmethacrylamide, N-(4-methoxycarbonylphenyl)methacrylamide, N,N-dimethylacrylamide and morpholinoacrylamide. The α -hydroxymethyl acrylate includes, for example, ethyl α -hydroxymethyl acrylate and cyclohexyl α -hydroxymethyl acrylate. The styrene derivative includes, for example, styrene and 4-tert-butylstyrene.

[0209] The "urethane resin" is preferably a urethane resin having, as a basic skeleton, a structural unit represented by a reaction product of at least one diisocyanate compound represented by the following Formula (1) and at least one diol compound represented by the following Formula (2).

[0210] OCN-X-NCO (1)

$\text{HO-L}^1\text{-OH}$ (2)

[0211] In Formulae (1) and (2), X and L^1 each independently represent a divalent organic residue.

[0212] At least one diol compound represented by Formula (2) preferably has an acid group. As a result, an alkali-soluble urethane resin is preferably produced by incorporating an acidic

group as a reaction product between the corresponding diisocyanate compound and the corresponding diol compound. According to this preparation method, an alkali-soluble urethane resin is easily produced, as compared to a case in which an acid group is substituted or incorporated at the desired side chain after reaction of the urethane resin.

[0213] In addition, at least one of the diisocyanate compound represented by Formula (1) and the diol compound represented by Formula (2) preferably has a crosslinkable group. Examples of the crosslinkable group include those mentioned above. As a result, an alkali-soluble urethane resin is preferably produced by incorporating a crosslinkable group as a reaction product between the corresponding diisocyanate compound and the corresponding diol compound. According to this preparation method, a urethane resin having a crosslinkable group is easily produced, as compared to a case in which a crosslinkable group is substituted or incorporated at the desired side chain after reaction of the urethane resin.

[0214] (1) Diisocyanate compound

In Formula (1), X is preferably a divalent aliphatic group, a divalent aromatic hydrocarbon group, or a group formed from a combination thereof, and the number of carbon atoms thereof is preferably 1 to 20, and more preferably 1 to 15. The divalent aliphatic group or divalent aromatic hydrocarbon group may each further contain a substituent which is unreactive with an isocyanate group.

[0215] Specific examples of the diisocyanate compound represented by Formula (1) include the following compounds.

That is, examples of the diisocyanate compound include aromatic diisocyanate compounds such as 2,4-tolylene diisocyanate, dimers of 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, p-xylylene diisocyanate, m-xylylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 1,5-naphthylene diisocyanate, and 3,3'-dimethylbiphenyl-4,4'-diisocyanate; aliphatic diisocyanate compounds such as hexamethylene diisocyanate, trimethyl hexamethylene diisocyanate, lysine diisocyanate, and dimer acid diisocyanate; alicyclic diisocyanate compounds such as isophorone diisocyanate, 4-4'methylene bis(cyclohexylisocyanate), methylcyclohexan-2,4 (or 2,6) diisocyanate, and 1,3-(isocyanatomethyl)cyclohexane; and diisocyanate compounds which are reaction products between a diol and a diisocyanate, such as adducts of 1 mole of 1,3-butylene glycol and 2 moles of tolylene diisocyanate.

[0216] When the diisocyanate compound represented by Formula (1) has a crosslinkable group, the diisocyanate compound is, for example, a product obtained by addition reaction of a triisocyanate compound and one equivalent of a monofunctional alcohol or monofunctional amine compound having a crosslinkable group (for example, ethylene unsaturated bond

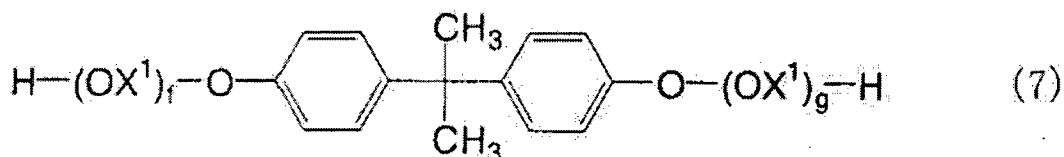
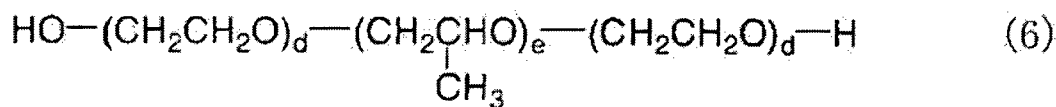
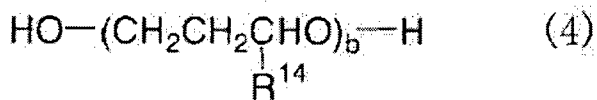
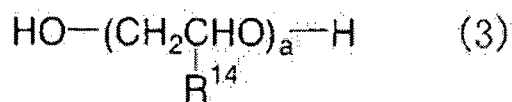
group). Specific examples of the triisocyanate compound, the monofunctional alcohol or monofunctional amine compound having a crosslinkable group include those described in paragraphs [0034], [0035], [0037] to [0040] of Japanese Patent No. 4401262, but are not limited thereto.

Specific examples of the diisocyanate compound having a crosslinkable group include those described in paragraphs [0042] to [0049] of Japanese Patent No. 4401262, but are not limited thereto.

[0217] (2) Diol compound

Examples of the diol compound represented by Formula (2) broadly include polyether diol compounds, polyester diol compounds, and polycarbonate diol compounds. Examples of the polyether diol compounds include compounds represented by the following Formulae (3), (4), (5), (6) and (7), and random copolymers between ethylene oxide and propylene oxide having a terminal hydroxyl group.

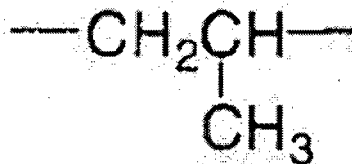
[0218]



[0219] In Formulae (3) to (7), R^{14} represents a hydrogen atom or a methyl group; and X^1 represents any one of the groups shown below; a, b, c, d, e, f and g each independently

represent an integer of 2 or more, and preferably an integer of 2 to 100; two d's may be the same as or different from each other; and two X¹s may be the same as or different from each other.

[0220]



[0221] Specific examples of polyether diol compounds represented by Formula (3) or (4) include the following compounds. That is, the examples include diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol, hexaethylene glycol, heptaethylene glycol, octaethylene glycol, di-1,2-propylene glycol, tri-1,2-propylene glycol, tetra-1,2-propylene glycol, hexa-1,2-propylene glycol, di-1,3-propylene glycol, tri-1,3-propylene glycol, tetra-1,3-propylene glycol, di-1,3-butylene glycol, tri-1,3-butylene glycol, hexa-1,3-butylene glycol, polyethylene glycol with a weight average molecular weight of 1,000, polyethylene glycol with a weight average molecular weight of 1,500, polyethylene glycol with a weight average molecular weight of 2,000, polyethylene glycol with a weight average molecular weight of 3,000, polyethylene glycol with a weight average molecular weight of 7,500, polypropylene glycol with a weight average molecular weight of 400, polypropylene glycol with a weight average molecular weight of 700, polypropylene glycol with a weight average molecular weight of 1,000, polypropylene glycol with a weight average molecular weight of 2,000, polypropylene glycol with a weight average molecular weight of 3,000, and polypropylene glycol with a weight average molecular weight of 4000.

[0222] Specific examples of polyether diol compound represented by Formula (5) include the following compounds. That is, the examples include PTMG650, PTMG1000, PTMG2000 and PTMG3000 (all trade names, manufactured by Sanyo Chemical Industries, Ltd.).

[0223] Specific examples of polyether diol compounds represented by Formula (6) include the following compounds. That is, the examples include NEWPOL PE-61, NEWPOL PE-62, NEWPOL PE-64, NEWPOL PE-68, NEWPOL PE-71, NEWPOL PE-74, NEWPOL PE-75, NEWPOL PE-78, NEWPOL PE-108, NEWPOL PE-128, and NEWPOL PE-61 (all trade names, manufactured by Sanyo Chemical Industries, Ltd.).

[0224] Specific examples of polyether diol compounds represented by Formula (7) include

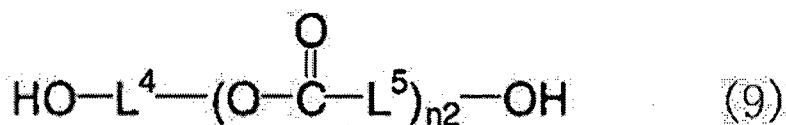
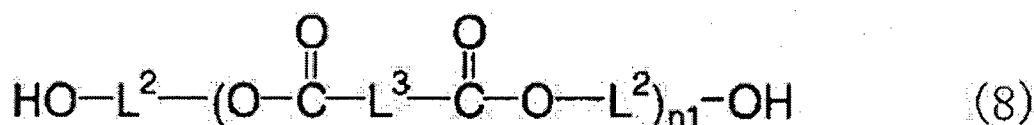
the following compounds. That is, the examples include NEWPOL BPE-20, NEWPOL BPE-20F, NEWPOL BPE-20NK, NEWPOL BPE-20T, NEWPOL BPE-20G, NEWPOL BPE-40, NEWPOL BPE-60, NEWPOL BPE-100, NEWPOL BPE-180, NEWPOL BPE-2P, NEWPOL BPE-23P, NEWPOL BPE-3P, and NEWPOL BPE-5P (all trade names, manufactured by Sanyo Chemical Industries, Ltd.).

[0225] Specific examples of the random copolymer of ethylene oxide and propylene oxide containing a terminal hydroxyl group include the following compounds.

That is, the examples include NEWPOL 50HB-100, NEWPOL 50HB-260, NEWPOL 50HB-400, NEWPOL 50HB-660, NEWPOL 50HB-2000 and NEWPOL 50HB-5100 (all trade names, manufactured by Sanyo Chemical Industries, Ltd.).

[0226] Examples of the polyester diol compounds include compounds represented by the following Formulae (8) and (9).

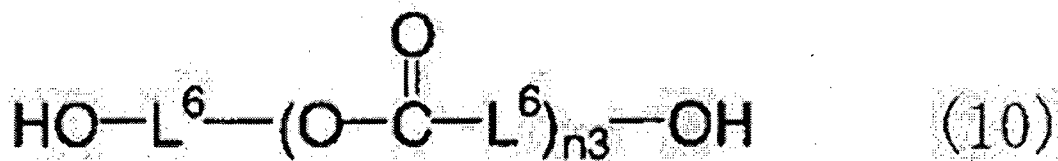
[0227]



[0228] In Formulae (8) and (9), L^2 , L^3 and L^4 each independently represent a divalent aliphatic or aromatic hydrocarbon group, and L^5 represents a divalent aliphatic hydrocarbon group. L^2 , L^3 and L^5 may be the same as or different from one another. Preferably, L^2 to L^4 each independently represent an alkylene group, an alkenylene group, an alkynylene group or an arylene group, and L^5 represents an alkylene group. Also, L^2 to L^5 may each contain another bond or functional group which is unreactive with an isocyanate group, such as an ether bond, a carbonyl bond, an ester bond, a cyano group, an olefin bond, a urethane bond, an amide group, an ureido group or a halogen atom. Furthermore, $n1$ and $n2$ each independently represent an integer of 2 or more, and preferably an integer of 2 to 100.

Examples of the polycarbonate diol compound include compounds represented by the following Formula (10).

[0229]



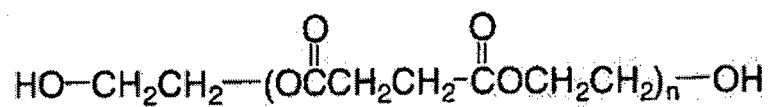
[0230] In Formula (10), L^6 s each independently represent a divalent aliphatic or aromatic hydrocarbon group, and may be the same as or different from each other. Preferably, L^6 represents an alkylene group, an alkenylene group, an alkynylene group or an arylene group. Also, L^6 may further contain another bond or functional group which is unreactive with an isocyanate group, such as an ether bond, a carbonyl group, an ester bond, a cyano group, an olefin bond, a urethane bond, an amide bond, an ureido group or a halogen atom.

Furthermore, $n3$ represents an integer of 2 or more, and preferably an integer of 2 to 100.

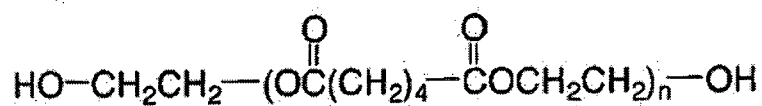
[0231] Specific examples of diol compounds represented by Formula (8), (9) or (10) include the following compounds (i.e., Exemplary Compound No. 1 to Exemplary Compound No. 18). In these specific examples, n represents an integer of 2 or more.

[0232]

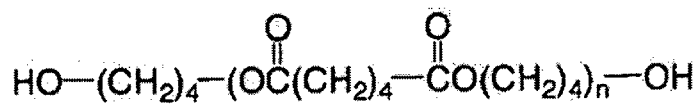
(No. 1)



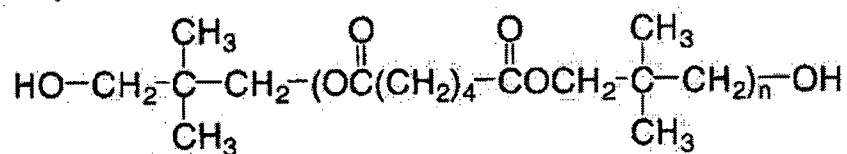
(No. 2)



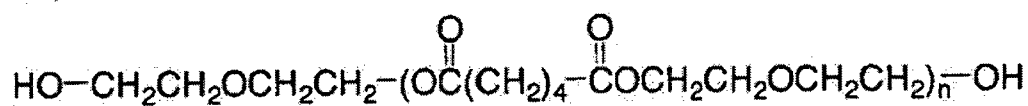
(No. 3)



(No. 4)

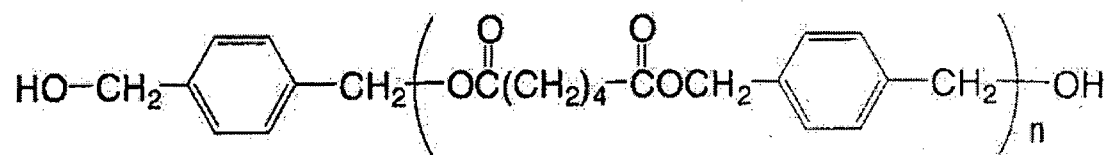


(No. 5)

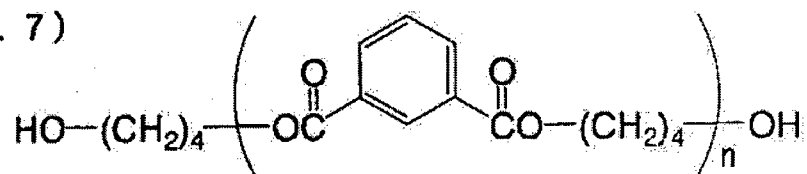


[0233]

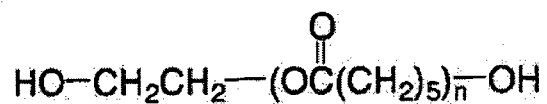
(No. 6)



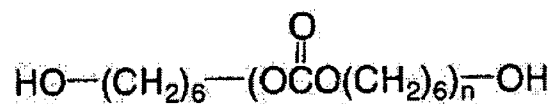
(No. 7)



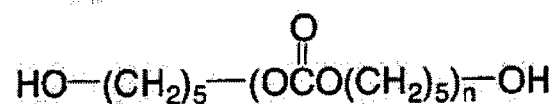
(No. 8)



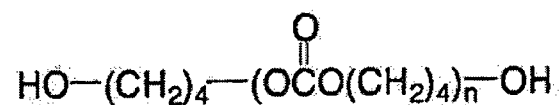
(No. 9)



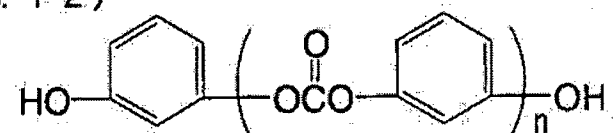
(No. 10)



(No. 11)

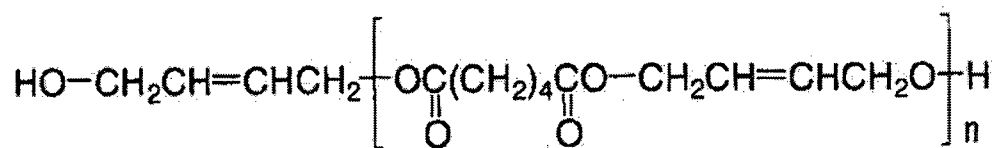


(No. 12)

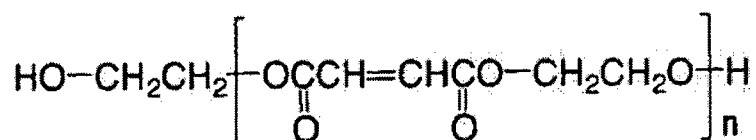


[0234]

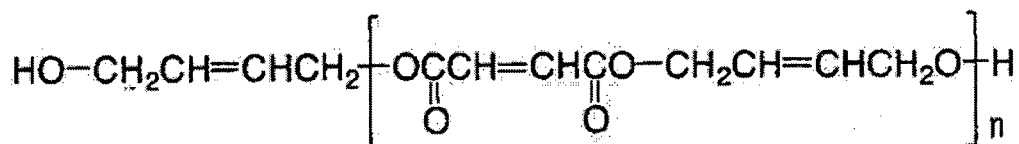
(No. 1 3)



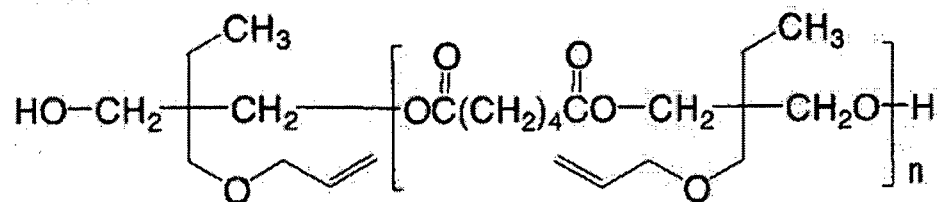
(No. 1 4)



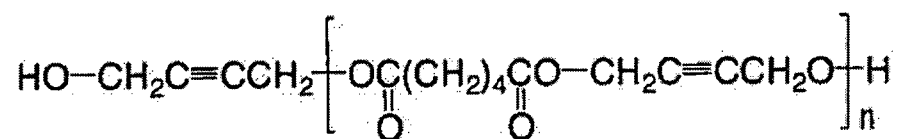
(No. 1 5)



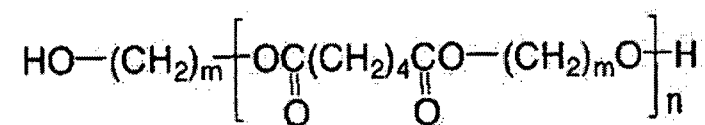
(No. 1 6)



(No. 1 7)



(No. 1 8)



$$m = 2, 4$$

[0235] The urethane resin may be synthesized using the diol compound in combination with a diol compound having a substituent which is unreactive with an isocyanate group. Examples of such a diol compound include the following compounds.

[0236] $\text{HO-L}^7\text{-O-CO-L}^8\text{-CO-O-L}^7\text{-OH}$ (11)

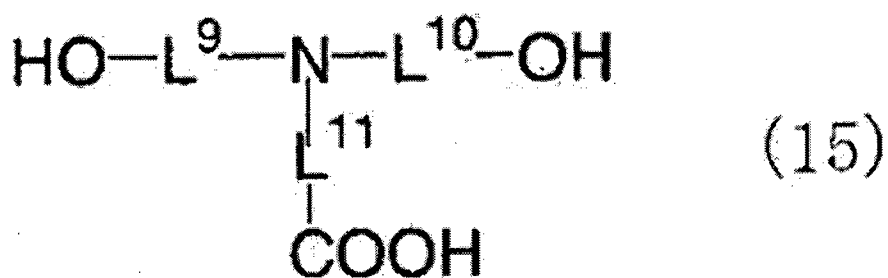
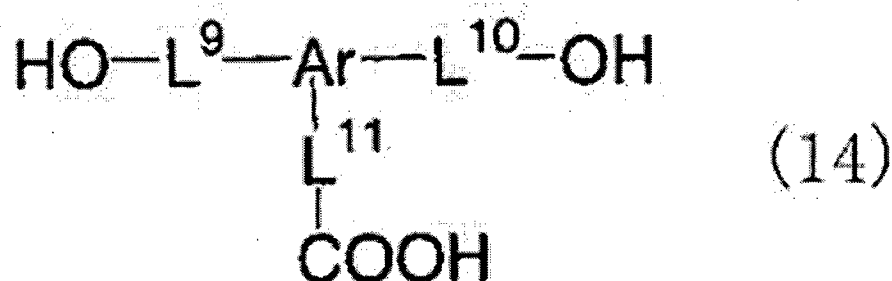
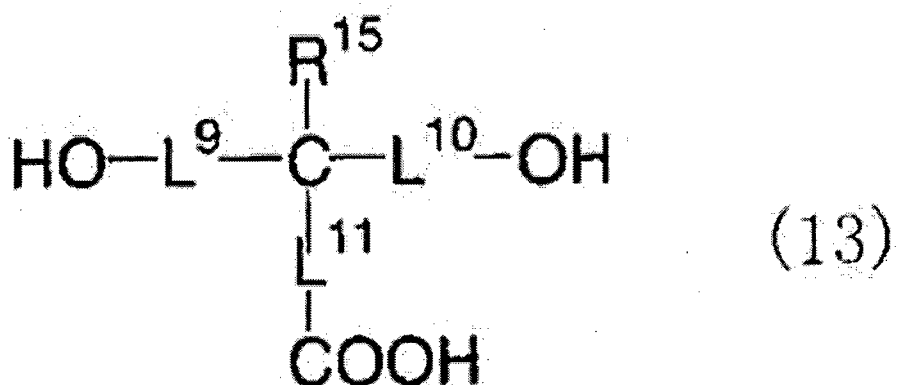
$\text{HO-L}^8\text{-CO-O-L}^7\text{-OH}$ (12)

[0237] In Formulae (11) and (12), L^7 and L^8 each independently represent a divalent aliphatic hydrocarbon group, a divalent aromatic hydrocarbon group or a divalent heterocyclic group, and plural L^7 's may be the same as or different from each other, and plural L^8 's may be the same as or different from each other. L^7 and L^8 may each further optionally contain another bond or functional group which is unreactive with an isocyanate group, such as a carbonyl group, an ester bond, a urethane bond, an amide bond, or a ureido group. In addition, L^7 and L^8 may form a ring.

The divalent aliphatic hydrocarbon group, aromatic hydrocarbon group or heterocyclic group may have or may not have a substituent, and examples of substituent include an alkyl group, an aralkyl group, an aryl group, an alkoxy group, an aryloxy group, and a halogen atom such as -F, -Cl, -Br or -I.

[0238] In addition, at least one of the diol compounds is preferably a diol compound having an acid group as a compound having a substituent which is unreactive with the isocyanate group. Specific examples of the acid group include the groups mentioned above, and a carboxylic group is preferred. Examples of diol compounds having a carboxylic group include the following compounds represented by Formulae (13) to (15).

[0239]



[0240] In Formulae (13) to (15), R^{15} represents a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, an alkoxy group, or aryloxy and preferably a hydrogen atom, an alkyl group having 1 to 8 carbon atoms, or an aryl group having 6 to 15 carbon atoms.

The alkyl group, the aralkyl group, the aryl group, the alkoxy group and the aryloxy group may each have a substituent, and examples of substituent include a cyano group, a nitro group, a halogen atom such as -F, -Cl, -Br or -I, -CONH₂, -COOR¹⁶, -OR¹⁶, -NHCONHR¹⁶, -NHCOOR¹⁶, -NHCOR¹⁶, and -OCONHR¹⁶ (in which R¹⁶ represents an alkyl group having 1

to 10 carbon atoms, or an aralkyl group having 7 to 15 carbon atoms).

L^9 , L^{10} and L^{11} may be the same as or different from each other, and each independently represent a single bond, a divalent aliphatic or aromatic hydrocarbon group, and preferably represent an alkylene group having 1 to 20 carbon atoms, an arylene group having 6 to 15 carbon atoms, and more preferably represent an alkylene group having 1 to 8 carbon atoms.

The divalent aliphatic or aromatic hydrocarbon group may or may not have a substituent, and examples substituent include an alkyl group, an aralkyl group, an aryl group, an alkoxy group, and a halogen atom.

Also, L^9 to L^{11} may further optionally contain a functional group which is unreactive with an isocyanate group, such as carbonyl, ester, urethane, amide, ureido, or ether group. In addition, two or three of R^{15} , L^7 , L^8 and L^9 may form a ring.

Ar represents a trivalent aromatic hydrocarbon group which may or may not have a substituent, and preferably represents an aromatic group having 6 to 15 carbon atoms.

[0241] Specific examples of diol compounds having a carboxyl group represented by Formulae (13) to (15) include the following compounds.

That is, examples include 3,5-dihydroxybenzoic acid, 2,2-bis(hydroxymethyl)propionic acid, 2,2-bis(2-hydroxyethyl)propionic acid, 2,2-bis(3-hydroxypropyl)propionic acid, bis(hydroxymethyl)acetic acid, bis(4-hydroxyphenyl)acetic acid, 2,2-bis(hydroxymethyl)butyric acid, 4,4-bis(4-hydroxyphenyl) pentanoic acid, tartaric acid, N,N-dihydroxyethyl glycine, and N,N-bis(2-hydroxyethyl)-3-carboxy-propionamide.

[0242] The carboxyl group is preferred from the viewpoint of imparting hydrogen bondability and alkali-solubility to a polyurethane resin.

A polyurethane resin containing a carboxyl group in a content of 0.5 meq/g to 4.0 meq/g, and more preferably 1.0 meq/g to 3.0 meq/g, is particularly preferred as a binder polymer used in the present invention.

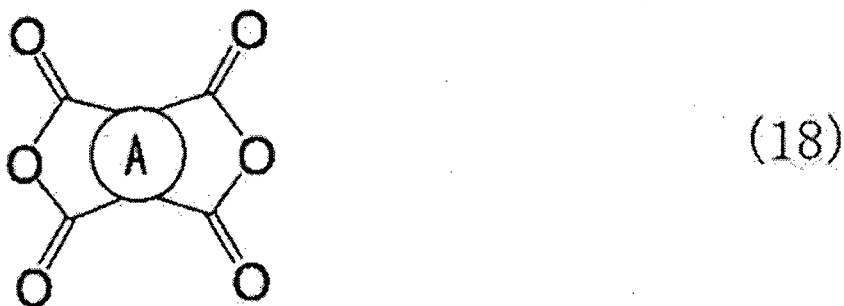
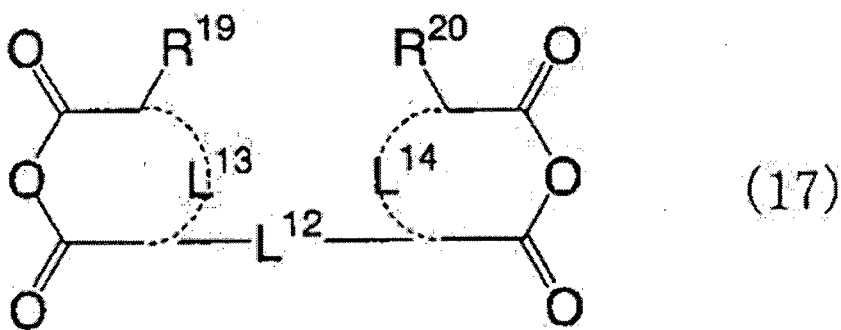
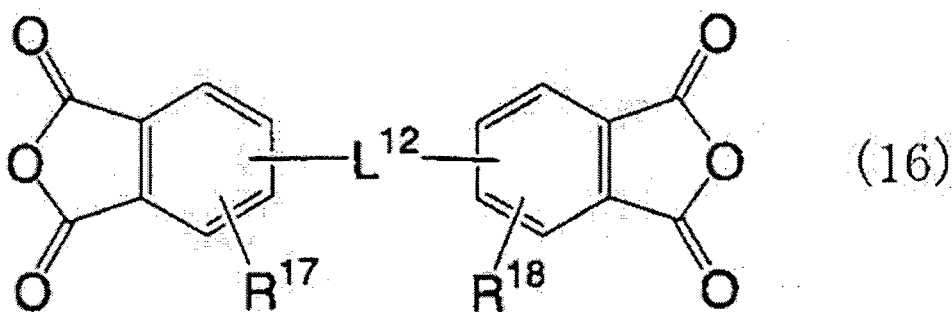
[0243] When the diol compound represented by Formula (2) has a crosslinkable group, use of a diol compound containing an unsaturated group is preferable for production of the polyurethane resin. Such a diol compound may be a commercially available product such as trimethylolpropane monoallyl ether, a product which may be easily produced by a reaction between a halogenated diol compound, triol compound, or amino diol compound with a carboxylic acid chloride, isocyanate, alcohol, amine, thiol or halogenated alkyl compound containing an unsaturated group. Specific examples of the diol compound having a crosslinkable group include those described in paragraphs of [0057] to [0066] of Japanese Patent No. 4401262, but are not limited thereto.

The compounds represented by Exemplary Compound No. 13 to No. 17 correspond to diol compounds represented by Formula (8), (9) or (10), and are diol compounds that have a crosslinkable group.

A polyurethane resin having a crosslinkable group (preferably, ethylenically unsaturated bond group) in a content of 0.5 meq/g or more, more preferably 1.0 meq/g to 3.0 meq/g is particularly preferred as a binder polymer used in the present invention.

[0244] In addition, the urethane resin may be synthesized using, in addition to the diol, a compound obtained by a ring-opening reaction of tetracarboxylic dianhydride represented by the following Formulae (16) to (18) with a diol compound.

[0245]



[0246] In Formulae (16) to (18), L^{12} represents a single bond, a divalent aliphatic or aromatic hydrocarbon group which may have a substituent (such as an alkyl group, an aralkyl group, an aryl group, an alkoxy group, a halogen group, an ester group or an amide group), -CO-, -SO-, -SO₂-, -O- or S-, and preferably represents a single bond, a divalent aliphatic hydrocarbon group having 1 to 15 carbon atoms, -CO-, -SO₂-, -O- or S-.

The divalent aliphatic or aromatic hydrocarbon group may or may not have a substituent, and examples substituent include an alkyl group, an aralkyl group, an aryl group, an alkoxy group, a halogen atom, an ester bond-containing group (for example, an alkylcarbonyloxy group, an alkyloxycarbonyl group, an arylcarbonyloxy group or an aryloxycarbonyl group), and an amide group.

R^{17} and R^{18} may be the same as or different from each other, and each independently represent a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, an alkoxy group, or a halogen group, and preferably represent a hydrogen atom, an alkyl group having 1 to 8 carbon atoms, an aryl group having 6 to 15 carbon atoms, an alkoxy group having 1 to 8 carbon atoms or a halogen group.

Also, two of L^{12} , R^{17} and R^{18} may be bonded together to form a ring.

[0247] R^{19} and R^{20} may be the same as or different from each other, and each independently represent a hydrogen atom, an alkyl group, an aralkyl group, an aryl group or a halogen group, and preferably represent a hydrogen atom, alkyl having 1 to 8 carbon atoms, or an aryl group having 6 to 15 carbon atoms.

Also, two of L^{12} , R^{19} and R^{20} may be bonded together to form a ring.

L^{13} and L^{14} may be the same as or different from each other, and each independently represent a single bond, a double bond, or a divalent aliphatic hydrocarbon group, and preferably represent a single bond, a double bond or a methylene group. A represents a mononuclear or multinuclear aromatic ring. Preferably, A represents an aromatic ring having 6 to 18 carbon atoms.

[0248] Specific examples of compounds represented by Formula (16), (17) or (18) include the following compounds. That is, the examples include pyromellitic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, 3,3',4,4'-diphenyl tetracarboxylic dianhydride, 2,3,6,7-naphthalene tetracarboxylic dianhydride, 1,4,5,8-naphthalene tetracarboxylic dianhydride, 4,4'-sulfonyldipthalic dianhydride, 2,2-bis(3,4-dicarboxylphenyl) propane dianhydride, bis(3,4-dicarboxylphenyl) ether dianhydride, 4,4'-[3,3'-(alkylphosphoryldiphenylene)-bis(iminocarbonyl)]dipthalic dianhydride;

[0249] aromatic tetracarboxylic dianhydride such as an adduct of hydroquinone diacetate and trimellitic anhydride, an adduct of diacetyldiamine and trimellitic anhydride; an alicyclic

tetracarboxylic dianhydride such as 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexy-1,2-dicarboxylic anhydride (EPICLON B-4400, trade name, made by DIC Corporation), 1,2,3,4-cyclopentane tetracarboxylic dianhydride, 1,2,4,5-cyclohexan tetracarboxylic dianhydride, tetrahydrofuran tetracarboxylic dianhydride; an aliphatic tetracarboxylic dianhydride such as 1,2,3,4-butane tetracarboxylic dianhydride, and 1,2,4,5-pentane tetracarboxylic dianhydride.

[0250] Methods for introducing from the compound in which this tetracarboxylic dianhydride is ring-opened with a diol compound into a polyurethane resin include the following methods.

a) Method of reacting the compound of an alcoholic terminal obtained by ring-opening tetracarboxylic dianhydride with a diol compound and a diisocyanate compound.

b) Method of reacting a urethane compound of an alcoholic terminal obtained by reacting a diisocyanate compound under the conditions of excess of a diol compound and tetracarboxylic dianhydride.

[0251] Examples of the diol compound used in the ring-opening reaction thereupon include the following compounds.

That is, examples thereof include ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, polyethylene glycol, polypropylene glycol, neopentyl glycol, 1,3-butylene glycol, 1,6-hexanediol, 2-butene-1,4-diol, 2,2,4-trimethyl-1,3-pentanediol, 1,4-bis- β -hydroxyethoxycyclohexane, cyclohexanedimethanol, tricyclodecanedimethanol, hydrogenated bisphenol A, hydrogenated bisphenol F, an ethylene oxide adduct of bisphenol A, an propylene oxide adduct of bisphenol A, an ethylene oxide adduct of bisphenol F, a propylene oxide adduct of bisphenol F, an ethylene oxide adduct of hydrogenated bisphenol A, a propylene oxide adduct of hydrogenated bisphenol A, hydroquinonedihydroxyethyl ether, p-xylylene glycol, dihydroxyethylsulfone, bis(2-hydroxyethyl)-2,4-tolylene dicarbamate, 2,4-tolylene-bis(2-hydroxyethylcarbamate), bis(2-hydroxyethyl)-m-xylylene dicarbamate, and bis(2-hydroxyethyl) isophthalate.

[0252] Hereinbefore, the urethane resin has been described and the urethane resin is synthesized by adding an active known catalyst reactive to the diisocyanate compound and the diol compound in a nonprotonic solvent, followed by heating. A molar ratio (Ma:Mb) of the diisocyanate compound and the diol compound used for synthesis is preferably 1:1 ~ 1.2:1 and the product with the desired physical property such as molecular weight or viscosity can be finally synthesized without leaving an isocyanate group by treating alcohols, amines or the like.

[0253] In addition, a urethane resin preferably has a crosslinkable group (for example,

unsaturated group) at an end or side chain of a polymer. By having a crosslinkable group (for example, unsaturated group) at an end or side chain of the polymer, cross-linkage reactivity between the polymerizable compound and the urethane resin, or between the urethane resins is improved and strength of a permanent pattern is enhanced. Accordingly, the unsaturated group particularly preferably has a carbon-carbon double bond from the viewpoint of the potentiality of cross-linkage.

[0254] Examples of methods for introducing a crosslinkable group into a polymer end include the following methods. That is, in the polyurethane resin synthesis process, a process for treating the remaining isocyanate group at a polymer end and alcohol, amine and the like is carried out using alcohol or amine having a crosslinkable group. Examples of the compound are the same as the exemplary compounds of monofunctional alcohols or monofunctional amine compounds having a crosslinkable group.

In addition, it is preferable that the crosslinkable group is incorporated into a side chain of the polymer, than an end of the polymer, from the viewpoint that the amount of incorporated cross-linking group can be increased and cross-linkage reactivity can be improved.

[0255] As a method for introducing a crosslinkable group into a main chain, there is a method in which a diol compound having an unsaturated group in a main chain direction is used for synthesis of a polyurethane resin. Specific examples of the diol compound having an unsaturated group in a main chain direction include the following compounds. That is, these compounds are cis-2-butene-1,4-diol, trans-2-butene-1,4-diol, polybutadiene diol and the like.

[0256] Alkali-soluble binders other than (meth)acryl resins and urethane resins are preferably acetal-modified polyvinyl alcohol-containing binder polymers having an acid group as described in EP Patent No. 993966, EP Patent No. 1204000 and JP-A No. 2001-318463 in terms of excellent balance between film strength and developability. In addition, other useful water-soluble linear organic polymers include polyvinyl pyrrolidone, polyethylene oxide and the like. Also, in order to improve strength of cured films, polyethers of alcohol-soluble nylon or 2,2-bis-(4-hydroxyphenyl)-propane, epichlorohydrin and the like are useful.

[0257] In particular, among these, [benzyl(meth)acrylate/(meth)acrylic acid, optionally, other adduct polymerizable vinyl monomer]copolymers, and [aryl(meth)acrylate/(meth)acrylic acid, optionally, other adduct polymerizable vinyl monomer]copolymers are preferable from the viewpoint of excellent balance between film strength, sensitivity and developability.

[0258] The weight average molecular weight of alkali-soluble binder which may be used for the light-shielding composition of the present invention is preferably 3,000 or more, more preferably 5,000 to 300,000, and most preferably 10,000 to 30,000, and the number average molecular weight thereof is preferably 1,000 or more, and more preferably 2,000 to 250,000. The polydispersion degree (i.e., weight average molecular weight/number average molecular weight) is preferably 1 or more, and more preferably from 1.1 to 10.

Such an alkali-soluble binder may be one of a random polymer, a block polymer, a graft polymer and the like.

[0259] The alkali-soluble binder may be synthesized by a conventional known method. Examples of the solvent used for synthesis include tetrahydrofuran, ethylene dichloride, cyclohexanone, propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, and butyl acetate. The solvents may be used alone or in combination of two or more types thereof.

[0260] The alkali-soluble binder may be used alone or in combination of two or more types thereof.

The content of alkali-soluble binder is preferably 5% by mass to 80% by mass, and more preferably 30% by mass to 70 % by mass, with respect to the total solid mass of the light-shielding composition of the present invention. When the content is within the above ranges, sensitivity of light exposure is good, processing time is shortened and superior TCT resistance is obtained.

[0261] *Ultraviolet absorber*

The light-shielding composition of the present invention preferably contains an ultraviolet absorber.

In a case in which the light-shielding composition contains an ultraviolet absorber, a rectangular-shaped pattern is favorably obtained when a lithography property is imparted to the light-shielding composition of the present invention.

The photosensitive composition of the present invention may contain an ultraviolet absorber.

Examples of ultraviolet absorbers include salicylate absorbers, benzophenone absorbers, benzotriazole absorbers, substituted acrylonitrile absorbers, and triazine ultraviolet absorbers.

[0262] Examples of salicylate ultraviolet absorbers include phenyl salicylate, p-octylphenyl salicylate, and p-t-butylphenyl salicylate. Examples of the benzophenone ultraviolet absorbers include 2,2'-dihydroxy-4-methoxy benzophenone, 2,2'-dihydroxy-4,4'-dimethoxy benzophenone, 2,2',4,4'-tetrahydroxy benzophenone, 2-hydroxy-4-methoxy benzophenone,

2,4-dihydroxy benzophenone, and 2-hydroxy-4-octoxybenzophenone. In addition, examples of the benzotriazole ultraviolet absorbers include 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3'-tert-amyl-5'-isobutylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3'-isobutyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3'-isobutyl-5'-propyl phenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3', 5'-di-tert-butylphenyl) benzotriazole, 2-(2'-hydroxy-5'-methylphenyl) benzotriazole, and 2-[2'-hydroxy-5'-(1,1,3,3-tetramethyl) phenyl]benzotriazole.

[0263] Examples of the substituted-acrylonitrile ultraviolet absorbers include ethyl 2-cyano-3,3-diphenyl acrylic acid, and 2-ethylhexyl-2-cyano-3,3-diphenylacrylic acid. In addition, examples of triazine ultraviolet absorbers include mono(hydroxyphenyl) triazine compounds such as 2-[4-[(2-hydroxy-3-dodecyloxypropyl)oxy]-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[4-[(2-hydroxy-3-tridecyloxypropyl)oxy]-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine; bis(hydroxyphenyl) triazine compounds such as 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-3-methyl-4-propyloxyphenyl)-6-(4-methylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-3-methyl-4-hexyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine; and tris(hydroxyphenyl) triazine compounds such as 2,4-bis(2-hydroxy-4-butoxyphenyl)-6-(2,4-dibutoxyphenyl)-1,3,5-triazine, 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, and 2,4,6-tris[2-hydroxy-4-(3-butoxy 2-hydroxypropyl oxy) phenyl]-1,3,5-triazine.

[0264] In the present invention, the various ultraviolet absorbers may be used alone or in combination of two or more types thereof.

The light-shielding composition of the present invention may contain or may not contain an ultraviolet absorber. When the composition contains an ultraviolet absorber, the content of ultraviolet absorber is preferably from 0.001 % by mass to 1% by mass, and more preferably, from 0.01% by mass to 0.8% by mass, with respect to the total solid mass of the light-shielding composition of the present invention.

[0265] *Surfactant*

Various surfactants may be added to the light-shielding composition of the invention, from the viewpoint of further improving the coat ability. Examples of the surfactants which may be used include fluorosurfactants, nonionic surfactants, cationic surfactants, anionic surfactants, silicone surfactants and the like.

In particular, silicone surfactants and fluorosurfactants are preferred, and fluorosurfactants are most preferred. When the light-shielding composition contains the surfactant, uniformity of the light-shielding composition after application is further improved.

That is, in a case in which films are formed using a coating solution using fluorosurfactant-containing light-shielding composition, interfacial tension between the surface to be coated and the coating solution is deteriorated, wettability of the surface to be coated is improved and coatability of the surface to be coated is thus improved. For this reason, it is effective in that a thin film with a uniform thickness in which non-uniformity in thickness is low is further preferably formed, although the thin film with a size of several micrometers is formed using a small amount of liquids.

[0266] The content of fluorine in the fluorosurfactant is preferably 3% by mass to 40% by mass, more preferably, 5% by mass to 30% by mass, and particularly preferably 7% by mass to 25% by mass. When the content of fluorine is within the above ranges, the fluorosurfactant may be effective from the viewpoints of uniformity of coating thickness and liquid saving property, and solubility in the light-shielding composition may also be satisfactory.

[0267] Examples of fluorosurfactants include MEGAFAC F171, MEGAFAC F172, MEGAFAC F173, MEGAFAC F176, MEGAFAC F177, MEGAFAC F141, MEGAFAC F142, MEGAFAC F143, MEGAFAC F144, MEGAFAC R30, MEGAFAC F437, MEGAFAC F475, MEGAFAC F479, MEGAFAC F482, MEGAFAC F554, MEGAFAC F780, MEGAFAC F781 (all trade names, manufactured by DIC Corporation), FLUORAD FC430, FLUORAD FC431, FLUORAD FC171 (all trade names, manufactured by Sumitomo 3M Ltd.), and SURFLON S-382, SURFLON SC-101, SURFLON SC-103, SURFLON SC-104, SURFLON SC-105, SURFLON SC1068, SURFLON SC-381, SURFLON SC-383, SURFLON S393, SURFLON KH-40 (all trade names, manufactured by Asahi Glass Co., Ltd.).

[0268] Specific examples of the nonionic surfactants include polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene nonyl phenyl ether, polyethylene glycol dilaurate, polyethylene glycol distearate, and sorbitan fatty acid ester such as PLURONIC L10, L31, L61, L62, 10R5, 17R2 and 25R2, and TETRONIC 304, 701, 704, 901, 904 and 150R1 (trade names, manufactured by BASF) and SOLSPERSE 20000 (trade name, manufactured by Lubrizol Corporation).

[0269] Examples of the cationic surfactants include a phthalocyanine derivative (trade name: EFKA No. 745, manufactured by Morishita & Co., Ltd.), an organosiloxane polymer KP341 (trade name, manufactured by Shin-Etsu Chemical Co., Ltd.), a (meth)acrylic acid (co)polymer (trade names: POLYFLOW No. 75, No. 90, No. 95, manufactured by Kyoeisha Chemical Co., Ltd.), and W001 (trade name, manufactured by Yusho Co., Ltd.).

[0270] Examples of the anionic surfactant include W004, W005 and W017 (trade names, manufactured by Yusho Co., Ltd.).

[0271] Examples of the silicone surfactant include "TORAY SILICONE DC3PA", "TORAY SILICONE SH7PA", "TORAY SILICONE DC11PA", "TORAY SILICONE SH21PA", "TORAY SILICONE SH28PA", "TORAY SILICONE SH29PA", "TORAY SILICONE SH30PA" and "TORAY SILICONE SH8400" (trade names, manufactured by Dow Corning Toray Co., Ltd.), TSF-4440, TSF-4300, TSF-4445, TSF-4460, and TSF-4452 (trade names, manufactured by Momentive Performance Materials Inc.), KP341, KF6001, and KF6002 (trade names, manufactured by Shin-Etsu Chemical Co., Ltd.), and BYK323 and BYK330 (trade names, manufactured by BYK Japan KK).

[0272] Only one surfactant may be used, or two or more surfactants may be used in combination.

The light-shielding composition may contain or may not contain a surfactant. When the light-shielding composition contains a surfactant, the content of surfactant is preferably from 0.001% by mass to 1% by mass, more preferably, from 0.01% by mass to 0.1% by mass, with respect to the total solid mass of the light-shielding composition of the present invention.

[0273] *Silane coupling agent*

The light-shielding composition of the present invention preferably contains a silane coupling agent.

When the light-shielding composition contains a silane coupling agent, adhesivity between the photosensitive layer (i.e., the light-shielding composition layer) and the substrate is further improved.

Examples of silane coupling agent which may be used for the light-shielding composition of the present invention include the silane coupling agents used for surface-treatment of respective particles mentioned above.

The silane coupling agent may be used alone or in combination of two or more types thereof.

[0274] *Cross-linking agent*

The light-shielding composition of the present invention may further contain a cross-linking agent in order to improve strength of permanent patterns.

The cross-linking agent is preferably a compound having a crosslinkable group and is more preferably a compound having two or more crosslinkable groups. Specific examples of the crosslinkable group include an oxetane group, a cyanate group, and the crosslinkable group which may be included in an alkali-soluble binder mentioned above. Among these, an epoxy group, an oxetane group or a cyanate group is preferred. That is, the cross-linking agent is particularly preferably an epoxy compound, an oxetane compound or a cyanate

compound.

Examples of the epoxy compound which may be suitably used as a cross-linking agent for the present invention include epoxy compounds containing at least two oxylane groups per molecule, epoxy compounds which contain at least two epoxy groups having an alkyl group at β -position per molecule, and the like.

[0275] Examples of the epoxy compounds containing at least two oxylane groups in a molecule include bixylenol epoxy compounds or bisphenol epoxy compounds (such as YX-4000, trade name, manufactured by Japan Epoxy Resin Co., Ltd.) or mixtures thereof, heterocyclic epoxy compounds containing an isocyanurate skeleton (such as TEPIC, trade name, manufactured by Nissan Chemical Industries, Ltd.; ARALDITE PT810, trade name, manufactured by BASF Corporation, Japan, and the like), bisphenol A epoxy compounds, novolac epoxy compounds, bisphenol F epoxy compound, hydrogen-containing bisphenol A epoxy compounds, bisphenol S epoxy compound, phenol novolac epoxy compounds, cresol novolac epoxy compound, halogenated epoxy compounds (for example, low-brominated epoxy compounds, high-halogenated epoxy compounds, brominated phenol novolac-type epoxy compounds and the like), allyl group-containing bisphenol A epoxy compounds, trisphenol methane epoxy compound, diphenyl dimethanol epoxy compounds, phenolbiphenylene epoxy compounds, dicyclopentadiene epoxy compounds (such as HP-7200, HP-7200 H, trade names, manufactured by DIC Corporation), glycidyl amine epoxy compounds (e.g., diamino diphenyl methane epoxy compounds, diglycidyl aniline, triglycidyl aminophenol and the like), glycidyl ester epoxy compounds (such as phthalic diglycidyl ester, adipic diglycidyl ester, hexahydrophthalic diglycidyl ester, dimer acid glycidyl ester etc.); hydantoin epoxy resins, alicyclic epoxy resins (such as 3,4-epoxy cyclohexenylmethyl-3',4'-epoxy cyclohexenyl carboxylate);

[0276] bis(3,4-epoxycyclohexylmethyl)adipate, dicyclopentadiene diepoxide, GT-300, GT-400, ZEHPE3150 (trade names, manufactured by Daniel Chemical Industries, Ltd.), imide cycloaliphatic epoxy resins, trihydroxyphenylmethane epoxy resins, bisphenol A novolac epoxy resins, tetraphenylethane epoxy resins, glycidyl phthalate resins, tetraglycidylxylenoylethane resins, naphthalene group-containing epoxy resins (naphthol aralkyl epoxy resins, naphthol novolac epoxy resins, tetrafunctional naphthalene epoxy resins, those commercially available include ESN-190, ESN-360 manufactured by Nippon Steel Chemical, HP-4032, EXA No. 4750, EXA No. 4700 manufactured by Dainippon Ink and Chemicals, Inc., etc.); reaction products obtained from a reaction between epichlorohydrin and a polyphenol compound which is obtained by addition reaction between a phenol compound and a diolefin compound such as divinylbenzene or dicyclopentadiene; a ring-

opening polymerization product of 4-vinylcyclohexene-1-oxide epoxidized with peracetic acid and the like; epoxy resins having a linear phosphorus containing structure; epoxy resins having cyclic phosphorus containing structure; α -methylstilbene liquid crystal epoxy resins, dibenzoyloxybenzene liquid crystal epoxy resins; azophenyl liquid crystal epoxy resins; azomethine phenyl liquid crystal epoxy resins; binaphthyl liquid crystal epoxy resins; azine epoxy resins; glycidyl methacrylate copolymer epoxy resins ("CP-50S" and "CP-50M" manufactured by NOF Corporation, etc.), and copolymerized epoxy resins between cyclohexyl maleimide and glycidyl methacrylate, bis(glycidyoxyphenyl)fluorine epoxy resins, and bis(glycidyoxyphenyl)adamantine epoxy resins. However, cross-linking agent is not limited to those stated above. These epoxy resins may be used alone or in combination of two or more types thereof.

[0277] Further, in addition to the epoxy compound containing at least two oxylane groups per molecule, an epoxy compound containing two epoxy groups per molecule, having an alkyl group at the β -position may be used. Compounds containing an epoxy group of which the β -position has been substituted by an alkyl group (more specifically a β -alkyl-substituted glycidyl group and the like) are particularly preferred.

The epoxy compound containing at least an epoxy group of which the β -position has an alkyl group may be such that all of the two or more epoxy groups contained in one molecule is a β -alkyl-substituted glycidyl group, or alternatively at least one epoxy group is a β -alkyl-substituted glycidyl group.

[0278] The oxetane compound is for example an oxetane resin which contains at least two oxetanyl groups per molecule.

Examples of the oxetane compound include bis[(3-methyl-3-oxetanylmethoxy)methyl]ether, bis[(3-ethyl-3-oxetanylmethoxy)methyl]ether, 1,4-bis[(3-methyl-3-oxetanylmethoxy)methyl]benzene, 1,4-bis[(3-ethyl-3-oxetanylmethoxy)methyl]benzene, (3-methyl-3-oxetanyl)methyl acrylate, (3-ethyl-3-oxetanyl)methyl acrylate, (3-methyl-3-oxetanyl)methyl methacrylate, (3-ethyl-3-oxetanyl)methyl methacrylate or oligomers thereof; or polyfunctional oxetanes such as copolymers thereof; and ether compounds prepared between a compound having an oxetane group and a resin having a hydroxyl group such as novolac resin, poly(p-hydroxystyrene), cardo bisphenols, calix-arenes, calix-resorcin arenes, and silsesquioxane; and copolymers between an unsaturated monomer having an oxetane ring and alkyl(meth)acrylate.

Examples of the bismaleimide compound include 4,4'-diphenylmethanebismaleimide, bis-(3-ethyl-5-methyl-4-maleimidephenyl)methane, 2,2'-bis-[4-(4-maleimidephenoxy)phenyl]propane and the like.

[0279] Examples of the cyanate compound include bis A cyanate compounds, bis F cyanate compounds, cresol novolac cyanate compounds, phenol novolac cyanate compounds and the like.

[0280] In addition, a melamine or a melamine derivative may be used as the cross-linking agent.

The light-shielding composition contains a melamine or melamine derivative, thus further improving adhesivity between the light-shielding composition layer and the metal wiring (in particular, copper line).

Examples of the melamine derivative include methylol melamine, alkylated methylol melamine (compounds in which a methylol group is etherified by methyl, ethyl, butyl and the like) and the like. Of these, hexamethoxy methyl melamine is most preferred in terms of adhesivity with metal wirings.

The cross-linking agent may be used alone or in combination of two or more types. The cross-linking agent is preferably melamine or alkylated methylol melamine, from the viewpoints of superior storage stability and effectiveness of improvement in surface hardness of the light-shielding composition layer or film strength of cured films. The cross-linking agent is particularly preferably melamine from the viewpoints of achieving higher levels of excellent suitability for thick film formation, excellent coating uniformity, excellent thickness uniformity on uneven surface, excellent high-temperature resistance, and excellent high-humidity resistance.

[0281] The light-shielding composition may contain or may not contain a cross-linking agent. When the light-shielding composition contains a cross-linking agent, the content of cross-linking agent is from 1% by mass to 40% by mass, and more preferably from 3% by mass to 20% by mass, based on the total solid mass of the light-shielding composition of the present invention.

[0282] *Curing accelerator*

The light-shielding composition of the present invention may contain a curing accelerator in order to facilitate thermal curing of the cross-linking agent such as an epoxy compound or an oxetane compound.

Examples of curing accelerator include amine compounds (such as dicyandimide, benzyldimethylamine, 4-(dimethylamino)-N,N-dimethylbenzylamine, 4-methoxy-N,N-dimethylbenzylamine, or 4-methyl-N,N-dimethylbenzylamine); quaternary ammonium salt compounds (such as triethylbenzyl ammonium chloride); block isocyanate compounds (such as dimethylamine); bicyclic amidine compounds of imidazole derivatives and salts thereof (such as imidazole, 2-methylimidazole, 2-ethylimidazole, 2-ethyl-4-methylimidazole, 2-

phenylimidazole, 4-phenylimidazole, 1-cyanoethyl-2-phenylimidazole, or 1-(2-cyanoethyl)-2-ethyl-4-methylimidazole); phosphorus compounds (such as triphenylphosphine); guanamine compounds (such as melamine, guanamine, acetoguanamine, or benzoguanamine); S-triazine derivatives (such as 2,4-diamino-6-methacryloyloxyethyl-S-triazine, 2-vinyl-2,4-diamino-S-triazine, 2-vinyl-4,6-diamino-S-triazine-isocyanuric acid adducts, or 2,4-diamino-6-methacryloyloxyethyl-S-triazine-isocyanuric acid adducts).

The curing accelerator is preferably melamine or dicyandiamide.

The curing accelerator may be used alone or in combination of two or more types thereof.

The light-shielding composition may or may not contain a curing accelerator. When the light-shielding composition contains a curing accelerator, the content of curing accelerator is generally 0.01 to 15% by mass with respect to the total solid of the light-shielding composition of the present invention.

[0283] *Elastomer*

The light-shielding composition of the present invention may further contain an elastomer.

In a case in which the light-shielding composition contains an elastomer, when the composition is used as a solder resist, adhesion of the print line plate with the conductor layer is further enhanced, and it is then possible to further improve the heat-resistance, heat-shock resistance, flexibility and toughness of a cured film.

[0284] The elastomer which may be used for the present invention is not particularly limited and may be suitably selected depending on the purpose. Examples thereof include styrene elastomers, olefin elastomers, urethane elastomers, polyester elastomers, polyamide elastomers, acrylic elastomers, and silicone elastomers. These elastomers are formed from a hard segment component and a soft segment component, and the hard segment component contributes to heat resistance and strength, and the soft segment component constitutes to flexibility and toughness. Among these, polyester elastomers are advantageous in terms of compatibility with other components.

[0285] Examples of the styrene elastomers include styrene-butadiene-styrene block copolymers, styrene-isoprene-styrene block copolymers, styrene-ethylene-butylene-styrene block copolymers and styrene-ethylene-propylene-styrene block copolymers. Examples of the components of the styrene elastomer include, in addition to styrene, styrene derivatives such as α -methylstyrene, 3-methylstyrene, 4-propylstyrene or 4-cyclohexylstyrene. Specific examples of styrene elastomers include TUFPRENE, SOLPRENE T, ASAPRENE T, and TUFTEC (all trade names, manufactured by Asahi Chemical Industries), ELASTOMER AR

(trade name, manufactured by Aron Kasei), KRAYTON G, CALIFLEX (trade names, manufactured by Shell Japan), JSR-TR, TSR-SIS, DAINALON (all trade names, manufactured by Nippon Synthetic Rubber), DENKA STR (trade name, manufactured by Denki Kagaku), QUINTAC (trade name, manufactured by Nippon Zeon), TPE-SB Series (trade name, manufactured by Sumitomo Chemicals), RUBBERON (trade name, manufactured by Mitsubishi Chemicals), SEPTON, HYBRAR (trade name, manufactured by Kuraray), SUMIFLEX (trade name, manufactured by Sumitomo Bakelite), LEOSTOMER, AND ACTIMER (trade name, both manufactured by Riken Vinyl Industries).

[0286] The olefin elastomer is a copolymer of an α -olefin having 2 to 20 carbon atoms, such as ethylene, propylene, 1-butene, 1-hexene or 4-methyl-pentene. Examples thereof include ethylene-propylene copolymers (EPR) and ethylene-propylene-diene copolymers (EPDM). Other examples of the olefin elastomer include copolymers of unconjugated dienes having 2 to 20 carbon atoms such as dicyclopentadiene, 1,4-hexadiene, cyclooctadiene, methylene norbornene, ethylidene norbornene, butadiene and isoprene with an α -olefin and epoxylated polybutadiene. Further, another olefin elastomer is carboxy-modified NBR which is a copolymer of methacrylic acid with butadiene-acrylonitrile copolymer. Further, other olefin elastomers are ethylene- α -olefin copolymer rubbers, ethylene- α -olefin unconjugated diene copolymer rubbers, propylene- α -olefin copolymer rubbers, and butene- α -olefin copolymer rubbers.

[0287] Specific examples of the olefin elastomer include MILASTOMER (trade name, manufactured by Mitsui Petrochemicals), EXACT (trade name, manufactured by Exxon Chemicals), ENGAGE (trade name, manufactured by Dow Chemicals), DYNABON HSBR which is a hydrogenated styrene-butadiene copolymer, NBR series which are butadiene-acrylonitrile copolymers, the XER series which are biterminal carboxy-modified butadiene-acrylonitrile copolymers having a crosslinking point (trade name, manufactured by Dainippon Ink Chemical Industries) and "BF-1000" (trade name, manufactured by Nippon Soda Co., Ltd.,) which is epoxylated polybutadiene in which polybutadiene is partially epoxylated.

[0288] A urethane elastomer includes a structural unit consisting of a hard segment of a low-molecular weight (short chain) diol and diisocyanate, and a soft segment of a high-molecular weight (long chain) diol and diisocyanate. Examples of high-molecular weight (long chain) diols are polypropylene glycol, polytetramethylene oxide, poly(1,4-butylene adipate), poly(ethylene-1,4-butylene adipate), polycaprolactone, poly(1,6-hexylene carbonate) and poly(1,6-hexylene neopentylene adipate). The number average molecular weight of the high-molecular weight (long chain) diol is preferably 500 to 10,000. Examples of short chain diols are ethylene glycol, propylene glycol, 1,4-butanediol and bisphenol A. The

number average molecular weight of the short chain diol is preferably 48 to 500. Specific examples of the urethane elastomers include PANDEX T-2185 or T-2983N (trade names, manufactured by Dainippon Ink Chemical Industries) and SIRAKTRAN E790.

[0289] A polyester elastomer is an elastomer obtained by polycondensation of a dicarboxylic acid or its derivative with a diol compound or its derivative. Examples of dicarboxylic acids are terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid and aromatic dicarboxylic acids wherein these rings are substituted by methyl groups, ethyl groups or phenyl groups; aliphatic dicarboxylic acids having 2 to 20 carbon atoms such as adipic acid, sebacic acid or dodecane dicarboxylic acid; and alicyclic dicarboxylic acids such as cyclohexane dicarboxylic acid. One, two or more of these compounds may be used. Examples of diol compounds are aliphatic or alicyclic diols, such as ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,10-decanediol and 1,4-cyclohexanediol; bisphenol A, bis-(4-hydroxyphenyl)-methane, bis-(4-hydroxy-3-methylphenyl)-propane, and resorcinol. One, two or more of these compounds may be used. A multi-block copolymer having an aromatic polyester (for example, polybutylene terephthalate) as the hard segment component, and an aliphatic polyester (for example, polytetramethylene glycol) as the soft segment component, can be used. Polyester elastomers are divided into a variety of grades of polyester elastomers depending on the type of hard segment and soft segment, ratio therebetween and difference in molecular weight therebetween and the like. Commercially available polyester elastomers are HITREL (trade name, manufactured by Dupont-Toray), PELPRENE (trade name, manufactured by Toyo Boseki) and ESPEL (trade name, manufactured by Hitachi Chemical Industries).

[0290] A polyamide elastomer is an elastomer including a hard segment of polyamide, and a soft segment of polyether or polyester, and may be roughly divided into two kinds such as a polyether block amide type and a polyether ester block amide type. Examples of polyamides are polyamide 6, polyamide 11 and polyamide 12, and examples of polyethers are polyoxyethylene, polyoxypropylene and polytetramethylene glycol. Specific examples of polyamide elastomers include UBE polyamide elastomers (trade name, manufactured by Ube Kosan), diamides (trade name, manufactured by Daicel Fuels), PEBAX (trade name, manufactured by Toray), GRILON ELY (trade name, manufactured by EMS Japan), NOVAMID (trade name, manufactured by Mitsubishi Chemicals) and GRILUX (trade name, manufactured by Dainippon Ink Chemical Industries).

[0291] An acrylic elastomer is an elastomer obtained by copolymerization of an acrylic ester such as ethyl acrylate, butyl acrylate, methoxyethyl acrylate and ethoxyethyl acrylate, with a monomer having an epoxy group, such as glycidyl methacrylate and allyl glycidyl ether,

and/or a vinyl monomer such as acrylonitrile or ethylene. Examples of acrylic elastomers include acrylonitrile-butyl acrylate copolymers, acrylonitrile-butyl acrylate-ethyl acrylate copolymers, and acrylonitrile-butyl acrylate-glycidyl methacrylate copolymers.

[0292] A silicone elastomer is an elastomer which contains an organopolysiloxane as their main component and examples thereof include polydimethylsiloxane, polymethylphenylsiloxane and polydiphenylsiloxane silicone elastomers. An elastomer wherein the organopolysiloxane has been modified by a vinyl group or an alkoxy group may also be used. Specific examples of silicone-based elastomers include silicone elastomers are the KE series (trade name, manufactured by Shin-Etsu Chemicals), SE series, CY series and SH series (trade name, manufactured by Dow Corning Toray Silicones).

[0293] In addition to the above elastomers, a rubber-modified epoxy resin may also be used. In the rubber-modified epoxy resin, at least part of the epoxy groups of the bisphenol F epoxy resin, bisphenol A epoxy resin, salicylaldehyde epoxy resin, phenol novolac epoxy resin, cresol novolac epoxy resin and the like are modified by biterminal carboxy-modified butadiene-acrylonitrile copolymer, or terminal amino-modified silicone rubber.

[0294] As the elastomer, a biterminal carboxy group-modified butadiene acrylonitrile copolymer, ESPEL (ESPEL 1612, ESPEL 1620, trade name, manufactured by Hitachi Chemical Industries) which is a polyester elastomer and epoxylated butadiene are preferred in terms of shear surface adhesion and resistance to thermal shock.

[0295] The light-shielding composition of the present invention may or may not contain an elastomer. When the light-shielding composition contains an elastomer, the content of elastomer in the light-shielding composition may be suitably selected without particular limitation depending on the purpose, and is preferably 0.5% by mass to 30% by mass, more preferably 1% by mass to 10% by mass, and particularly preferably 3% by mass to 8% by mass, based on the solid content of the composition. When the content of elastomer is within the above ranges, it is advantageous in that shear surface adhesion and resistance to thermal shock are further improved.

[0296] *Other components*

The light-shielding composition of the present invention may further contain other components, in addition to the essential components or preferred additives, depending on the purpose, so long as the effects of the present invention are impaired.

Examples of other components that can be used in combination include a thermosetting accelerator, a heat-polymerization inhibitor, a plasticizer, a colorant (coloring pigment or pigments) and the like. In addition, an adhesion accelerator and other adjuvant (such as a conductive particle, a defoaming agent, a flame retardant, a leveling agent, a

peeling accelerator, an antioxidant, a flavoring, a surface tension modifier and a chain transfer agent) may be used in combination for the surface of base material.

By the light-shielding composition suitably containing these components, properties of film of the desired solder resist such as stability, photographic property and physical properties can be controlled.

[0297] The heat-polymerization inhibitor is described in detail in for example the paragraphs [0101] to [0102] of JP-A No. 2008-250074.

The plasticizer is described in detail in for example the paragraphs [0103] to [0104] of JP-A No. 2008-250074.

The colorant is described in detail in for example the paragraphs [0105] to [0106] of JP-A No. 2008-250074 or [0038], [0039] of JP-A No. 2009-205029.

The adhesion accelerator is described in detail in for example the paragraphs [0107] to [0109] of JP-A No. 2008-250074.

All of the additives described in the publications are useful for light-shielding composition of the present invention.

[0298] The light-shielding composition of the present invention is prepared by mixing (A) one of a light-shielding particle and a light-shielding dye, a (B) first filler, and a (C) second filler and, optionally, mixing a (D) polymerizable compound, a (E) photopolymerization initiator, and other components.

It is preferable for the preparation of the light-shielding composition of the present invention, to previously prepare a dispersion of the light-shielding particle, a dispersion of the (B) first filler and a dispersion of the (C) second filler.

The light-shielding composition of the present invention thus obtained is preferably filtered through a filter to remove foreign materials and reduce defects. Any filter may be used without particular limitation so long as it is conventionally used for filtering. Examples thereof include filters composed of a fluoro resin such as PTFE (polytetrafluoroethylene), a polyamide resin such as nylon-6 and nylon-6,6, polyethylene, or a polyolefin resin such as polypropylene (PP) (including polyolefin resin with high-density and ultrahigh molecular weight). Of these materials, polypropylene (including high-density polypropylene) is preferred.

[0299] The pore diameter of the filter is suitably from about 0.01 μm to about 7.0 μm , preferably from about 0.01 μm to about 2.5 μm , and more preferably from about 0.01 μm to 1.5 μm . When the pore diameter is within the above ranges, fine foreign materials which are contaminated in a dissolved pigment or dye and which inhibit preparation of a uniform and even light-shielding composition in the following process are reliably removed.

A combination of different filters may be used when a filter is to be used. At this time, filtration using a first filter may be performed once or twice. In a case in which two or more filtering processes are performed due to use in combination with other filter, the pore diameter of the second filter is preferably larger than that of the first filter. In addition, a combination of first filters having different pore diameters from each other within the above ranges may be used. The pore diameter may be determined based on the nominal value of the filter maker. Examples of commercially available filters include various filters manufactured by Japan Pole Co., Ltd., ADVANTEC MFS, Inc., Entegris Inc., Japan (former, Mykrolis Corporation) or Kitz Microfilter Corp.

The second filter may be a filter which is composed of the same material as the first filter. The pore diameter of the second filter is from about 0.5 μm to about 7.0 μm , preferably from about 2.5 μm to 7.0 μm , and more preferably from about 4.5 μm to about 6.0 μm . When the pore diameter is within the above ranges, foreign materials which are contaminated in the mixed solution and which inhibit formation of a uniform and even light-shielding composition during the subsequent process are removed while remaining in component particles contained in the light-shielding composition.

For example, the first filter may be used only to filter the each particle dispersion and may be used secondarily to filter a light-shielding composition containing other components. [0300] The solid concentration in the light-shielding composition of the present invention is preferably from 5% by mass to 90% by mass, more preferably from 20% by mass to 80% by mass, and most preferably from 40% by mass to 60 % by mass.

The light-shielding composition of the present invention may be used without any particularly limitation, and the composition may be applicable to solder resists, light-shielding films of the back surface of a silicon substrate in a solid-state imaging device, light-shielding films of a wafer level lens and the like. The application to a solder resist is preferred.

[0301] When the light-shielding composition of the present invention is used as a solder resist, the solid concentration is preferably from 30% by mass to 80% by mass, more preferably from 35% by mass to 70% by mass, and most preferably from 40% by mass to 60% mass, to form a thin film having a relatively high thickness.

In addition, the viscosity of the light-shielding composition of the present invention is preferably from 1 mPa·s to 3,000 mPa·s, more preferably from 10 mPa·s to 2,000 mPa·s, and most preferably from 100 mPa·s to 1,500 mPa·s.

When the light-shielding composition of the present invention is used as a solder resist, the viscosity is preferably from 10 mPa·s to 3,000 mPa·s, more preferably from 400 mPa·s to 1,500 mPa·s, and most preferably from 400 mPa·s to 1,000 mPa·s, from the

viewpoints of film formability and uniform coating.

[0302] The present invention also relates to a photosensitive layer formed from the light-shielding composition of the present invention. Since the photosensitive layer is formed from a light-shielding composition of the present invention, the photosensitive layer is capable of forming a pattern that exhibits a superior blocking property in an infrared range and a superior light-transmittance in a visible light region, has a desired shape and has a superior durability (durability to high-temperature and high-humidity or adhesion to substrate, and the like).

In addition, the present invention also relates to a permanent pattern formed from the light-shielding composition of the present invention. The permanent pattern of the present invention may be obtained by subjecting the photosensitive layer formed from the light-shielding composition of the present invention to light exposure and alkali development. Since the light-shielding composition of the invention is used, the permanent pattern is a pattern that exhibits a superior blocking property in an infrared range and a superior light-transmittance in a visible light region, has a desired shape and has a superior durability (durability to high-temperature and high-humidity or adhesion to substrate, and the like).

[0303] The present invention also relates to a method for forming a pattern, including: forming a photosensitive layer using the light-shielding composition of the present invention as a solder resist on a substrate; exposing the photosensitive layer to light to cure an exposed region; and developing the light-exposed photosensitive layer using alkali to form a pattern.

[0304] Hereinafter, a method for forming a permanent pattern such as a solder resist pattern using the light-shielding composition of the present invention will be described in detail. The following description associated with the type or used amount of solvent for preparing a coating solution, coating method of the coating solution, thickness of photosensitive layer, light exposure or other processes is not limited to use thereof for a solder resist. In addition, hereinafter, a case in which a photosensitive layer (light-shielding composition layer) is formed using the light-shielding composition is provided as one example.

[0305] *Photosensitive layer*

In order to form a solder resist pattern, first, a photosensitive layer is formed using the light-shielding composition of the present invention. The photosensitive layer is not particularly limited so long as it contains the light-shielding composition. The film thickness, layer structure and the like may be suitably determined depending on the purpose.

[0306] For example, the photosensitive layer is formed by dissolving, emulsifying or dispersing the light-shielding composition of the present invention in water or a solvent, to prepare a coating solution; directly applying the coating solution on a support; and drying the

coated support.

[0307] The solvent used for preparing the coating solution is not particularly limited. The solvent may be suitably determined from those capable of uniformly dissolving or dispersing respective components of the light-shielding composition of the present invention, depending on the purpose. Examples thereof include alcohols such as methanol, ethanol, normal-propanol, isopropanol, normal-butanol, sec-butanol or normal-hexanol; ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, diisobutylketone, cyclohexanone, or cyclopentanone; esters such as ethyl acetate, butyl acetate, normal-amyl acetate, methyl sulfate, ethyl propionate, dimethyl phthalate, ethyl benzoate, propylene glycol monomethyl ether acetate, or methoxy propyl acetate; aromatic hydrocarbons such as toluene, xylene, benzene, or ethylbenzene; halogenated hydrocarbons such as carbon tetrachloride, trichloroethylene, chloroform, 1,1,1-trichloroethane, methylene chloride, or monochlorobenzene; ethers such as tetrahydrofuran, diethyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 1-methoxy-2-propanol, or propylene glycol monomethyl ether; and dimethylformamide, dimethylacetamide, dimethylsulfoxide, sulfolane and the like. These solvents may be used alone or in combination of two or more types thereof. In addition, a known surfactant may be also added.

[0308] A method for applying the coating solution on a support is not particularly limited and may be suitably selected depending on the purpose. Examples of the method include coating using a spin coater, a slit-and-spin coater, a slit coater, a roll coater, a die coater, a curtain coater, an inkjet method or the like. Of these methods, a spin coater is particularly preferable to obtain "suitability for thick film formation", which is an object of the present invention.

In addition, drying conditions of thin film depend on the type of respective components and the solvent and contents thereof, and is generally at a temperature of 60°C to 150°C for about 30 seconds to about 15 minutes.

[0309] The thickness of the photosensitive layer is not particularly limited and may be suitably determined depending on the purpose. For example, the thickness is preferably 1 μm to 100 μm , more preferably, 2 μm to 50 μm , and particularly preferably, 4 μm to 30 μm .

[0310] *Method for forming solder resist pattern*

A method for forming a permanent solder resist pattern using the light-shielding composition for a solder resist of the present invention includes at least a light exposure process, and may further include a developing process in which conditions therefor are appropriately selected as needed, and other processes. In the present invention, the term "light exposure" or "exposure" used herein means irradiation with light having any one of

various wavelengths as well as irradiation with an electron beam or a radiation such as i-ray.

[0311] *Light exposure process*

In a light exposure process, the photosensitive layer formed from the light-shielding composition layer is subjected to light exposure using a mask. In this process, only an irradiated region (i.e., exposed region) is cured.

The light exposure is preferably carried out by irradiation of a radiation. Examples of preferred types of radiation which may be used for light exposure include in particular, electron beams, KrF, ArF, ultraviolet rays such as g-ray, h-ray or i-ray, and visible light. In particular, KrF, g-ray, h-ray and i-ray are preferred.

The light exposure may be carried out by light exposure using a stepper, light exposure using a high-pressure mercury lamp, or the like.

The light exposure amount is preferably 5 mJ/cm^2 to $3,000 \text{ mJ/cm}^2$, more preferably 10 mJ/cm^2 to $2,000 \text{ mJ/cm}^2$, and most preferably, 50 mJ/cm^2 to $1,000 \text{ mJ/cm}^2$.

[0312] *Other processes*

The other processes may be suitably selected depending on the purpose without particular limitation, and examples thereof include a surface treatment process, a development process, a curing treatment process, and a post-light exposure process.

[0313] *Development process*

After the light exposure process, an alkali development process is performed, and a region which has not been exposed to light during the light exposure process is eluted to an aqueous alkali solution. As a result, only a region which is cured by light exposure (i.e., exposed region) remains, and a patterned solder resist having a light blocking property is formed.

A development solution is preferably an organic alkali development solution which does not cause damage to the underlying circuits. A development temperature is generally 20°C to 40°C , and a development time is 10 seconds to 180 seconds.

[0314] Examples of the alkali used for a development solution include organic alkaline compounds such as ammonia water, ethylamine, diethylamine, dimethylethanolamine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, choline, pyrrole, piperidine, and 1,8-diazabicyclo-[5, 4, 0]-7-undecene, and it is preferable to use an aqueous alkali solution obtained by diluting with pure water such that a concentration of any one of the above-mentioned organic alkaline compounds in the aqueous alkali solution is 0.001 % by mass to 10 % by mass, and preferably 0.01 % by mass to 1 % by mass. When the development solution is such an aqueous alkali solution, the development solution is generally washed with pure water after development.

[0315] *Curing treatment process*

The curing treatment process is a process in which the photosensitive layer provided with the pattern which has been formed in the development process is cured. As a result of this process, mechanical strength of a permanent pattern is improved.

The curing treatment process may be suitably determined depending on the purpose without particular limitation, and considerably preferred examples thereof include entire-surface light exposure and entire-surface heating.

[0316] The entire-surface light exposure may be, for example, carried out by subjecting the entire surface of the laminate having a patterned photosensitive layer formed in the development process, to light exposure. As a result of the entire-surface light exposure, curing of polymerizable components in the light-shielding composition constituting the photosensitive layer is facilitated, and the permanent pattern is further cured, and mechanical strength and durability are improved.

An apparatus used for the entire-surface light exposure may be suitably selected depending on the purpose without particular limitation, and preferred examples thereof include UV light exposure apparatuses such as ultrahigh-pressure mercury lamps.

[0317] The entire-surface heating process may be, for example, carried out by heating the entire surface of the laminate having a patterned photosensitive layer formed in the development process. As a result of entire-surface heating, strength of a patterned film is improved.

The heating temperature during entire-surface heating is preferably 120°C to 250°C, and more preferably 150°C to 220°C. When the heating temperature is 120°C or higher, film strength is improved through heating, and when the heating temperature is 250°C or lower, the resin in the light-shielding composition is degraded, and the film is prevented from being weakened and brittle.

The heating time during entire-surface heating is preferably 3 minutes to 180 minutes, and more preferably 5 minutes to 120 minutes.

An apparatus for entire-surface heating may be suitably selected from known apparatuses depending on the purpose without any particular limitation, and examples thereof include dry ovens, hot plates, and IR heaters.

[0318] The patterned resist film thus formed exhibits an excellent infrared light shielding property, and is thus applicable to various applications. The light-shielding composition of the present invention exhibits an excellent light shielding property in an infrared range and an excellent light-transmission in an ultraviolet region to a visible light region, thus enabling formation of a pattern having an excellent shape. Furthermore, since the formed pattern (i.e.,

cured film) exhibits an excellent infrared light shielding property, the pattern is applicable to devices having photodiodes and having sensitivity in an infrared range, in particular, is useful for formation of a solder resist for a solid-state imaging device.

[0319] As mentioned above, the light-shielding composition of the present invention is useful for formation of a solder resist, as well as a light-shielding film for the back surface of a silicon substrate in a solid-state imaging device and a light-shielding film for a wafer level lens.

[0320] As such, the present invention also relates to a solid-state imaging device that has a permanent pattern formed from the light-shielding composition of the present invention.

[0321] Hereinafter, a solid-state imaging device according to an exemplary embodiment of the present invention will be described with reference to FIGS. 1 and 2, but the present invention is not limited to the following specific examples.

In addition, common elements throughout FIGS. 1 and 2 are represented by a common reference numeral.

In addition, in the description, "on", "above", "over" and "upward" mean a side far from a silicon substrate 10, and "under", "below" and "downward" mean a side near to the silicon substrate 10.

[0322] FIG. 1 is a schematic view illustrating the configuration of a camera module including a solid-state imaging device according to an exemplary embodiment of the invention.

The camera module 200 shown in FIG. 1 is connected to a circuit substrate 70 as a mounting substrate, via solder balls 60 as connection members.

Specifically, the camera module 200 includes: a solid-state imaging device substrate 100 having at least a silicon substrate and an imaging device unit provided on a first main surface of the silicon substrate; a glass substrate 30 (light-transmissive substrate) arranged above the first main surface of the solid-state imaging device substrate 100; an infrared cut filter 42 arranged above the glass substrate 30; a lens holder 50 which includes an imaging lens 40 in an internal space thereof, and is arranged above the glass substrate 30 and the infrared cut filter 42; and a light-shielding electromagnetic shield 44 which surrounds the solid-state imaging device substrate 100 and the glass substrate 30. Respective members are connected via adhesives 20, 41, 43 and 45.

In the camera module 200, light (incident light: $h\nu$) incident from the outside is transmitted through the image lens 40, the infrared cut filter 42 and the glass substrate 30 in this order, and then reaches the imaging device unit of the solid-state imaging device substrate 100.

The camera module 200 is connected to the circuit substrate 70 via the solder balls 60 (connection material) provided at the second main surface of the solid-state imaging device substrate 100.

[0323] FIG. 2 is an enlarged cross-sectional view illustrating the solid-state imaging device substrate 100 of FIG. 1.

The solid-state imaging device substrate 100 includes: a silicon substrate 10 as a substrate; imaging devices 12; an interlayer insulating film 13; a base layer 14; a red color filter 15R; a green color filter 15G; a blue color filter 15B; an overcoat 16; micro lenses 17; a light-shielding film 18; an insulating film 22; a metal electrode 23; a solder resist layer 24; an inner electrode 26; and an element surface electrode 27.

[0324] First, a configuration at the first main surface of the solid-state imaging device substrate 100 is mainly described.

As shown in FIG. 2, the imaging device unit in which the imaging devices 12 such as a CCD or CMOS are arranged in plurality in a two-dimensional manner is provided at the first main surface side of the silicon substrate 10 which is a base body of the solid-state imaging device substrate 100.

On the imaging devices 12 in the imaging device unit, the interlayered insulating layer 13 is formed, and the base layer 14 is formed on the interlayered insulating layer 13. Further, the red color filter 15R, the green color filter 15G, and the blue color filter 15B (hereinbelow, collectively referred to as "color filters 15" in some cases) are respectively disposed on the base layer 14 to correspond to the imaging devices 12.

A light-shielding film (not shown) may be provided in the boundaries of the red color filter 15R, the green color filter 15G, and the blue color filter 15B, and the periphery of the imaging device unit. This light-shielding film may be manufactured by, for example, the light-shielding composition of the invention.

The overcoat 16 is formed on the color filters 15, and the micro-lenses 17 are formed on the overcoat 16 to correspond to the imaging devices 12 (color filters 15).

[0325] Also, peripheral circuits (not shown) and the internal electrode 126 are provided in the periphery of the imaging device unit on the first main surface, and the internal electrode 26 is connected to the imaging devices 12 via the peripheral circuits.

The element surface electrode 27 is formed on the internal electrode 26 via the interlayered insulating layer 13. In the interlayered insulating layer 13 between the internal electrode 26 and the element surface electrode 27, a contact plug (not shown) for electrically connecting them to each other is formed. The element surface electrode 27 is used to apply voltages or to read signals via the contact plug and the internal electrode 26.

The base layer 14 is formed on the element surface electrode 27. The overcoat 16 is formed on the base layer 14. The base layer 14 and the overcoat 16 formed on the element surface electrode 27 are opened to form a pad aperture which exposes a portion of the element surface electrode 27.

[0326] The above description is for the configuration at the first main surface side of the solid-state imaging device substrate 100.

In the first main surface side of the solid-state imaging device substrate 100, an adhesive 20 is provided in the vicinity of the imaging device unit, and the solid-state imaging device substrate 100 is adhered to the glass substrate 30 via the adhesive 20.

[0327] The silicon substrate 10 has a through-hole penetrating the silicon substrate 10, and a penetrating electrode which is a portion of the metal electrode 23 is disposed in the through-hole. The imaging device unit is electrically connected to the circuit board 70 via the penetrating electrode.

[0328] Next, a configuration at the second main surface side of the solid-state imaging device substrate 100 is mainly described.

In the second main surface side, the insulating layer 22 is formed from the second main surface through the inner wall of the through-hole.

On the insulating layer 22, the patterned metal electrode 23 is provided from the region on the second main surface of the silicon substrate 10 to the inside of the through-hole. The metal electrode 23 is an electrode for connecting the imaging device unit of the solid-state imaging device substrate 100 to the circuit board 70.

The penetrating electrode is a part formed inside the through-hole, of the metal electrode 23. The penetrating electrode penetrates the silicon substrate 10 and a portion of the interlayered insulating layer, reaches the lower side of the internal electrode 26 and is electrically connected to the internal electrode 26.

[0329] Further, in the second main surface side, the solder resist layer 24 (i.e., protection insulating layer) is provided which covers the second main surface where the metal electrode 23 is formed, and has an aperture for exposing a portion of the metal electrode 23.

Also, in the second main surface side, the light-shielding film 18 is provided which covers the second main surface where the solder resist layer 24 is formed, and has the aperture for exposing a portion of the metal electrode 23.

In this configuration, (1) the light-shielding solder resist layer in which the light-shielding film 18 and the solder resist layer 24 are formed into a single layer may be formed from the light-shielding composition of the invention, or (2) the light-shielding film 18 and the solder resist layer 24 may be formed into respective layers, and the light-shielding film

18 may be formed from the light-shielding composition of the invention.

In Fig. 2, although the light-shielding film 18 is patterned so as to cover a portion of the metal electrode 23 and expose the remaining portion, it may be patterned so as to expose the entire metal electrode 23 (the same is applied to the patterning of the solder resist layer 24).

[0330] A solder ball 60 as a connection member is provided on the exposed metal electrode 23, and the metal electrode 23 of the solid-state imaging device substrate 100 is electrically connected to a connection electrode (not shown) of the circuit substrate 70 via the solder ball 60.

[0331] The solid-state imaging device substrate 100 has been described above. Respective members, other than the light-shielding film 18 in the solid-state imaging device substrate 100 may be formed by a known method such as the method disclosed in paragraphs [0033] to [0068] of JP-A No. 2009-158863, or the method disclosed in paragraphs [0036] to [0065] of JP-A No. 2009-99591.

The light-shielding film 18 may be formed by the method for manufacturing the light-shielding film according to the present invention.

The interlayer insulating film 13 is, for example, a SiO₂ film or SiN film formed by sputtering, chemical vapor deposition (CVD) or the like.

The color filters 15 are, for example, formed by photolithography using a known color resist.

The overcoat 16 and the base layer 14 are, for example, formed by photolithography using a known resist for forming an organic interlayer film.

The micro-lenses 17 are, for example, formed by photolithography using a styrene resin or the like.

When a light-shielding solder resist layer is formed as a single layer formed by combining the solder resist layer 24 and the light-shielding film 18, the light-shielding solder resist layer may be formed using the light-shielding composition of the present invention.

The solder balls 60 may be formed using Sn-Pb (eutetic), 95 Pb-Sn (high-leaded high-melting point solder), or Sn-Ag, Sn-Cu or Sn-Ag-Cu as a Pb free solder. The solder balls 60 may be formed to each have a sphere shape having a diameter of 100 μm to 1,000 μm, and preferably 150 μm to 700 μm.

The inner electrode 26 and the element surface electrode 27 may each be formed in the form of a metal electrode of Cu or the like, by chemical mechanical polishing (CMP), or photolithography and etching.

The metal electrode 23 may be formed as a metal electrode formed from Cu, Au, Al,

Ni, W, Pt, Mo, a Cu compound, a W compound, a Mo compound or the like, by sputtering, photolithography, etching, and/or electroplating. The metal electrode 23 may have a single-layer structure or a multilayer structure including two or more layers. The film thickness of the metal electrode 23 may be 0.1 μm to 20 μm , and preferably 0.1 μm to 10 μm . The silicon substrate 10 is not particularly limited, and may be a silicon substrate which has been thinned by peeling the back surface thereof. The thickness of substrate is not limited, and a silicon wafer having a thickness of 20 μm to 200 μm , and preferably 30 μm to 150 μm may be used.

The through hole of the silicon substrate 10 may be formed by photolithography and reactive ion etching (RIE).

[0332] As described above, although the solid-state imaging device substrate 100 which is a specific example of an embodiment is described with reference to FIGS. 1 and 2, the embodiments of the present invention are not limited to those illustrated in FIGS. 1 and 2, and a configuration is not particularly limited as long as the configuration has the metal electrode and the light-shielding film in the back surface side.

EXAMPLES

[0333] Hereinafter, examples of the present invention will be described, but the present invention is not limited thereto. Hereinbelow, "part(s)" and "%" are in terms of mass, unless otherwise noted.

[0334] *Preparation of filler dispersion b-1*

First, 31 parts by mass of a silica filler (SO-C1, trade name, manufactured by Admatechs Co., Ltd.; having a particle diameter which indicates a maximum value in a particle diameter distribution thereof of 250 nm), 58 parts by mass of a resin (ACA230AA, trade name, manufactured by Daicel-cytec Company Ltd.; solid content of 55%; solvent: propylene glycol monomethyl ether), and 11 parts by mass of hexamethoxymethylmelamine were previously mixed, and were then dispersed in a motor mill M-50 (trade name, manufactured by Eiger Co., Ltd.) using zirconia beads having a diameter of 1.0 mm at a peripheral speed of 9 m/s for 1.5 hours, thereby obtaining a filler dispersion b-1.

[0335] *Preparation of filler dispersion b-2*

First, 31 parts by mass of a silica filler (SO-C2, trade name, manufactured by Admatechs Co., Ltd.; having a particle diameter which indicates a maximum value in a particle diameter distribution of 500 nm), 58 parts by mass of a resin (ACA230AA, trade name, manufactured by Daicel-cytec Company Ltd.; solid content of 55%; solvent: propylene glycol monomethyl ether), and 11 parts by mass of hexamethoxymethylmelamine were

previously mixed, and were then dispersed in a motor mill M-50 (trade name, manufactured by Eiger Co., Ltd.) using zirconia beads having a diameter of 1.0 mm at a peripheral speed of 9 m/s for 1.5 hours, thereby obtaining a filler dispersion b-2.

[0336] *Preparation of filler dispersion b-3*

First, 31 parts by mass of a silica filler (SO-C3, trade name, manufactured by Admatechs Co., Ltd.; having a particle diameter which indicates a maximum value in a particle diameter distribution of 900 nm), 58 parts by mass of a resin (ACA230AA, trade name, manufactured by Daicel-cytec Company Ltd.; solid content of 55%; solvent: propylene glycol monomethyl ether), and 11 parts by mass of hexamethoxymethylmelamine were previously mixed, and were then dispersed in a motor mill M-50 (trade name, manufactured by Eiger Co., Ltd.) using zirconia beads having a diameter of 1.0 mm at a peripheral speed of 9 m/s for 1.5 hours, thereby obtaining a filler dispersion b-3.

[0337] *Preparation of filler dispersion b-4*

First, 31 parts by mass of a silica filler (SO-C5, trade name, manufactured by Admatechs Co., Ltd.; having a particle diameter which indicates a maximum value in a particle diameter distribution of 1,600 nm), 58 parts by mass of a resin (ACA230AA, trade name, manufactured by Daicel-cytec Company Ltd.; solid content of 55%; solvent: propylene glycol monomethyl ether), and 11 parts by mass of hexamethoxymethylmelamine were previously mixed, and were then dispersed in a motor mill M-50 (trade name, manufactured by Eiger Co., Ltd.) using zirconia beads having a diameter of 1.0 mm at a peripheral speed of 9 m/s for 1.5 hours, thereby obtaining a filler dispersion b-4.

[0338] *Preparation of filler dispersion b-5*

First, 31 parts by mass of a silica filler (SO-C6, trade name, manufactured by Admatechs Co., Ltd.; having a particle diameter which indicates a maximum value in a particle diameter distribution of 2,200 nm), 58 parts by mass of a resin (ACA230AA, trade name, manufactured by Daicel-cytec Company Ltd.; solid content of 55%; solvent: propylene glycol monomethyl ether), and 11 parts by mass of hexamethoxymethylmelamine were previously mixed, and were then dispersed in a motor mill M-50 (trade name, manufactured by Eiger Co., Ltd.) using zirconia beads having a diameter of 1.0 mm at a peripheral speed of 9 m/s for 1.5 hours, thereby obtaining a filler dispersion b-5.

[0339] *Preparation of filler dispersion b-6*

First, 31 parts by mass of a silica filler (QS-04, trade name, manufactured by Mitsubishi Rayon Co., Ltd.; having a particle diameter which indicates a maximum value in a particle diameter distribution of 4,000 nm), 58 parts by mass of a resin (ACA230AA, trade name, manufactured by Daicel-cytec Company Ltd.; solid content of 55%; solvent: propylene

glycol monomethyl ether), and 11 parts by mass of hexamethoxymethylmelamine were previously mixed, and were then dispersed in a motor mill M-50 (trade name, manufactured by Eiger Co., Ltd.) using zirconia beads having a diameter of 1.0 mm at a peripheral speed of 9 m/s for 1.5 hours, thereby obtaining a filler dispersion b-6.

[0340] *Preparation of filler dispersion b-7*

First, 31 parts by mass of a silica filler (SO-C1, trade name, manufactured by Admatechs Co., Ltd.; having a particle diameter which indicates a maximum value in a particle diameter distribution of 250 nm), 58 parts by mass of a resin (ACA230AA, trade name, manufactured by Daicel-cytec Company Ltd.; solid content of 55%; solvent: propylene glycol monomethyl ether), and 11 parts by mass of melamine were previously mixed, and were then dispersed in a motor mill M-50 (trade name, manufactured by Eiger Co., Ltd.) using zirconia beads having a diameter of 1.0 mm at a peripheral speed of 9 m/s for 1.5 hours, thereby obtaining a filler dispersion b-7.

[0341] *Preparation of filler dispersion c-1*

First, 7 parts by mass of a silica filler (Aerosil50, trade name, manufactured by Nippon Aerosil Co., Ltd.; having a particle diameter which indicates a maximum value in a particle diameter distribution of 17 nm) and 93 parts by mass of a resin (ACA230AA, trade name, manufactured by Daicel-cytec Company Ltd.; solid content of 55%; solvent: propylene glycol monomethyl ether) were previously mixed, and were then dispersed in a motor mill M-50 (trade name, manufactured by Eiger Co., Ltd.) using zirconia beads having a diameter of 1.0 mm at a peripheral speed of 9 m/s for 1.5 hours, thereby obtaining a filler dispersion c-1.

[0342] *Preparation of filler dispersion c-2*

First, 100 g of a silica filler (Aerosil300, trade name, manufactured by Nippon Aerosil Co., Ltd.; having a particle diameter which indicates a maximum value in a particle diameter distribution of 7 nm) and 500g of ion exchange water were weighed. To these, 1.5g of a 2.38% by mass aqueous tetramethylammonium hydroxide solution was added. The mixture was sonicated using a Branson 8510 (trade name, manufactured by Emerson Co., Ltd., Japan) for one hour. The resulting aqueous solution was centrifuged using an OptimaL-90 K at 10,000 rpm for 15 minutes, and the supernatant was collected and the solvent was distilled off using a rotary evaporator N-1000 (trade name, manufactured by Tokyo Rikakikai Co., Ltd.), thereby obtaining a silica filler having a particle diameter of 4 nm which is a maximum value in a particle diameter distribution.

Then, 7 parts by mass of the thus-obtained silica filler and 93 parts by mass of the resin (ACA230AA, trade name, manufactured by Daicel-cytec Company Ltd.; solid content of 55%; solvent: propylene glycol monomethyl ether) were previously mixed, and were then

dispersed in a motor mill M-50 (trade name, manufactured by Eiger Co., Ltd.) using zirconia beads having a diameter of 1.0 mm at a peripheral speed of 9 m/s. However, since mill moving unit of the apparatus was stopped due to high viscosity of the solution, the treatment was quitted at this stage.

[0343] *Preparation of filler dispersion c-3*

First, 7 parts by mass of a silica filler (AerosilOX50, trade name, manufactured by Nippon Aerosil Co., Ltd.; having a particle diameter which indicates a maximum value in a particle diameter distribution of 40 nm) and 93 parts by mass of a resin (ACA230AA which is mentioned above) were previously mixed, and were then dispersed in a motor mill M-50 (trade name, manufactured by Eiger Co., Ltd.) using zirconia beads having a diameter of 1.0 mm at a peripheral speed of 9 m/s for 1.5 hours, thereby obtaining a filler dispersion c-3.

[0344] *Preparation of filler dispersion c-4*

First, 51.15 parts by mass of a solid content obtained by reprecipitation of ACA230AA (trade name, manufactured by Daicel-cytec Company Ltd.; solid content of 55%; solvent: propylene glycol monomethyl ether) was mixed with 41.85 parts by mass of propylene glycol monomethyl ether acetate and 7 parts by mass of a silica filler (AEROSIL 50, trade name, manufactured by Nippon Aerosil Co., Ltd.; having a particle diameter which indicates a maximum value in a particle diameter distribution of 17 nm). Then, the resulting mixture was dispersed in a motor mill M-50 (trade name, manufactured by Eiger Co., Ltd.) using zirconia beads having a diameter of 1.0 mm at a peripheral speed of 9 m/s for 1.5 hours, thereby obtaining a filler dispersion c-4.

[0345] *Preparation of filler dispersion c-5*

First, 51.15 parts by mass of a solid content obtained by reprecipitation of ACA230AA (trade name, manufactured by Daicel-cytec Company Ltd.; solid content of 55%; solvent: propylene glycol monomethyl ether) was mixed with 41.85 parts by mass of butyl acetate and 7 parts by mass of a silica filler (AEROSIL 50, trade name, manufactured by Nippon Aerosil Co., Ltd.; having a particle diameter which indicates a maximum value in a particle diameter distribution of 17 nm). Then, the resulting mixture was dispersed in a motor mill M-50 (trade name, manufactured by Eiger Co., Ltd.) using zirconia beads having a diameter of 1.0 mm at a peripheral speed of 9 m/s for 1.5 hours, thereby obtaining a filler dispersion c-5.

[0346] *Preparation of filler dispersion c-6*

First, 51.15 parts by mass of a solid content obtained by reprecipitation of ACA230AA (trade name, manufactured by Daicel-cytec Company Ltd.; solid content of 55%; solvent: propylene glycol monomethyl ether) was mixed with 2.15 parts by mass of

dipropylene glycol monomethyl ether, 2.2 parts by mass of butyl acetate, 37.5 parts by mass of propylene glycol monomethyl ether acetate, and 7 parts by mass of a silica filler (Aerosil 50, trade name, manufactured by Nippon Aerosil Co., Ltd.; having a particle diameter which indicates a maximum value in a particle diameter distribution of 17 nm). Then, the resulting mixture was dispersed in a motor mill M-50 (trade name, manufactured by Eiger Co., Ltd.) using zirconia beads having a diameter of 1.0 mm at a peripheral speed of 9 m/s for 1.5 hours, thereby obtaining a filler dispersion c-6.

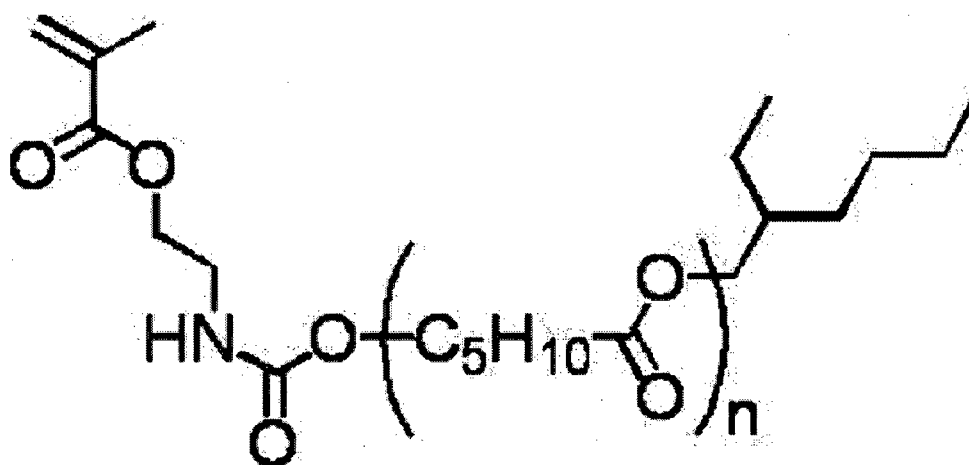
[0347] *Preparation of titanium black A*

First, 100 g of titanium oxide having a particle diameter of 15 nm (MT-150A, trade name, manufactured by Tayca Corporation), 25 g of a silica particle having a BET surface area of 300 m²/g (AEROPERL (registered trademark) 300/30, manufactured by Evonik Monosilane Japan Co., Ltd.), and 100 g of DISPERBYK 190 (trade name, manufactured by BYK Japan KK.) were weighed. To these, 71 g of ion exchange water was added, and the resulting mixture was treated using a MAZERSTARKK-400W (trade name, manufactured by KURABO) at an orbital rotation rate of 1,360 rpm and a spin rotation rate of 1,047 rpm for 20 minutes, to obtain a homogeneous mixture aqueous solution. The thus-obtained aqueous solution was charged into a quartz vessel, and heated using a small rotary kiln (manufactured by Motoyama Co., Ltd.) under an oxygen atmosphere at 920°C. Thereafter, the atmosphere was substituted with nitrogen, and an ammonia gas was blew at the same temperature at a rate of 100 mL/min for 5 hours, to perform a nitrogen reduction treatment. After this treatment, the collected powder was ground in a mortar to obtain titanium black A in the powder form.

[0348] *Synthesis of dispersant 1*

First, 600.0 g of ϵ -caprolactone and 22.8 g of 2-ethyl-1-hexanol were put in a 500 mL three-necked flask, and dissolved with stirring while nitrogen purging. Then, 0.1 g of monobutyl tin oxide was added thereto, followed by heating to 100°C. After 8 hours, elimination of the raw materials was confirmed by gas chromatography, and the mixture was cooled to 80°C. Then, 0.1 g of 2,6-di-*t*-butyl-4-methylphenol was added thereto, followed by addition of 27.2 g of 2-methacryloyloxyethyl isocyanate. After 5 hours, elimination of the raw materials were confirmed by ¹H-NMR, and the mixture was cooled to 80°C, thereby obtaining 200 g of a precursor M1 in the solid form (having the structure below; n = 30). Identification of precursor M1 was carried out by ¹H-NMR, IR, and mass analysis.

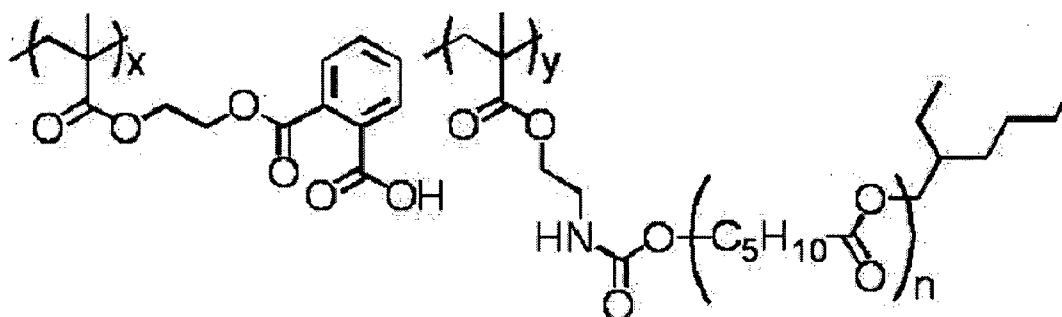
[0349]



M1

[0350] Next, 30.0 g of the precursor M1, 70.0 g of NK ESTER CB-1 (2-methacryloyloxyethyl phthalate; trade name, manufactured by Shin-Nakamura Chemical Co., Ltd.), 2.3 g of dodecyl mercaptan, and 233.3 g of propylene glycol monomethyl ether acetate were put in a nitrogen-substituted three-necked flask, and stirred using a stirrer (THREE-ONE MOTOR, trade name, manufactured by SHINTO Scientific Co., Ltd.) and heated to 75°C while nitrogen was blew into the flask. Then, 0.2 g of dimethyl 2,2-azobis(2-methyl propionate) (V-601, trade name, manufactured by Wako Pure Chemical Industries, Ltd.) was added thereto, followed by stirring with heating at 75°C for 2 hours. After 2 hours, 0.2 g of V-601 was further added, followed by stirring with heating for 3 hours, thereby obtaining a 30% by mass solution of a dispersant 1 having the following structure.

[0351]



Dispersant 1 (n = 30)

[0352] The composition ratio, acid value and weight average molecular weight (Mw) of the dispersant 1 were as follows. The weight average molecular weight was measured by gel permeation chromatography (GPC) and calculated based on polystyrene. GPC was carried

out using a HLC-8020GPC (trade name, manufactured by Tosoh Co., Ltd.) with TSKgel SUPER HZM-H, TSKgel SUPER HZ4000, and TSKgel SUPER HZ200 (trade names, manufactured by Tosoh Co., Ltd.) as columns.

- Composition ratio: x = 35 (% by mass), y = 65 (% by mass)
- Acid value: 80 mgKOH/g
- Mw: 30, 000

[0353] *Preparation of titanium black dispersion 2*

The components mentioned below in the "Composition 1" were mixed using a stirrer (EUROSTAR, trade name, manufactured by IKA Co., Ltd.) for 15 minutes, thereby obtaining a dispersion.

(Composition 1)

- Titanium black A prepared as above: 25 parts
- Dispersant: dispersant 1 prepared as above (30 mass% aqueous solution): 25 parts
- Organic solvent: propylene glycol monomethyl ether acetate (hereinafter, may be referred to as "PGMEA"): 130 parts

[0354] The dispersion thus obtained was subjected to a dispersion treatment under the conditions mentioned below using an Ultra Apex mill UAM015 (trade name, manufactured by Kotobuki Industries Co., Ltd.), thereby obtaining a titanium black dispersion 2 (solid concentration: 18.0% by mass). The particle diameter of titanium black dispersion 2 which indicates a maximum value in a particle diameter distribution was 19 nm.

[0355] (Dispersion conditions)

- Bead diameter: $\phi 0.05$ mm
- Bead filling ratio: 75 vol%
- Mill peripheral speed: 8 m/sec
- Amount of mixed solution to be dispersed: 500 g
- Circulating flow rate (pump feed amount): 13 kg/hour
- Temperature of treatment solution: 25 to 30°C
- Cooling water: tap water
- Volume of a bead mill cyclic channel: 0.15 L
- Number of passing: 90 passes

[0356] *Preparation of carbon black dispersion 3*

The following composition I was subjected to a high-viscosity dispersion treatment using a two-roll mill, thereby obtaining a dispersion.

Then, a mixture of the following composition II was added to the thus-obtained dispersion, and the resulting mixture was stirred using a homogenizer at 3,000 rpm for 3

hours. The obtained mixed solution was finely dispersed using a disperser (trade name: DISPERMAT, manufactured by GETZMANN GmbH) using zirconia beads having a particle diameter of 0.3 mm for 4 hours, thereby obtaining a carbon black dispersion 3 (solid concentration: 18.0% by mass).

[0357] (Composition I)

- Carbon black (Pigment Black 7) having a particle diameter of 15 nm which indicates a maximum value in a particle diameter distribution: 23 parts by mass
- 45% by mass PGMEA solution of benzyl methacrylate/methacrylic acid copolymer (copolymerization ratio of benzyl methacrylate/methacrylic acid = 67/33 (mol%), Mw: 28,000): 22 parts by mass
- SOLSPERSE 5000 (trade name, manufactured by The Lubrizol Corporation): 1.2 parts by mass

[0358] (Composition II)

- 45 % by mass PGMEA solution of benzyl methacrylate/methacrylic acid copolymer (benzyl methacrylate unit/methacrylic acid unit = 67/33 (mol%), Mw: 28,000): 22 parts by mass
- PGMEA: 176 parts by mass

[0359] *Example 1*

The compositions mentioned below were mixed, and filtered (under the conditions mentioned below), thereby obtaining a light-shielding composition of Example 1.

- (A) Light-shielding particle: 18.5 % by mass dispersion of YMF-02 (trade name, manufactured by Sumitomo Metal Mining; cesium tungsten oxide ($\text{Cs}_{0.33}\text{WO}_3$), having a particle diameter which indicates a maximum value in a particle diameter distribution of 20 nm): 26.97 parts by mass
- (D) Polymerizable compound: A-DCP (trade name, manufactured by Shin-Nakamura Chemical Co., Ltd.; difunctional polymerizable compound): 5.2 parts by mass
- (E) Photopolymerization initiator: IRGACURE 907 (trade name, manufactured by BASF Corporation, Japan.): 1.24 parts by mass
- Sensitizing agent: KAYACURE DETX-S (thioxanthone compound, trade name, manufactured by Nippon Kayaku Co., Ltd.): 0.37 parts by mass
- UV absorber: DPO (trade name, manufactured by FUJIFILM Fine Chemicals Co., Ltd.): 0.08 parts by mass
- Silane coupling agent: KBM-503 (trade name, manufactured by Shin-Etsu silicone Co., Ltd.): 2.30 parts by mass
- Surfactant: MEGAFAC F-780 (trade name, manufactured by DIC Corporation):

- | | |
|--|---------------------|
| | 0.14 parts by mass |
| · (B) Filler dispersion b-1 (mentioned above): | 1.50 parts by mass |
| · (C) Filler dispersion c-1 (mentioned above): | 61.40 parts by mass |

[0360] *Filtration conditions*

In the above mentioned filtration treatment, PROFILE-STAR (trade name, manufactured by Poll Corporation, Japan; made of polypropylene; filtration accuracy: 1.5 μm) was used as a first filter, and HDC-II (trade name, manufactured by Poll Corporation, Japan; made of high-density polypropylene; filtration accuracy: 6.0 μm) was used as a second filter.

[0361] *Example 2*

A light-shielding composition of Example 2 was prepared in the same manner as in Example 1 except that the dispersion of the light-shielding particles used in Example 1 was changed to the titanium black dispersion 2.

[0362] *Example 3*

A light-shielding composition of Example 3 was prepared in the same manner as in Example 1 except that the dispersion of the light-shielding particles used in Example 1 was changed to the carbon black dispersion 3.

[0363] *Example 4*

A light-shielding composition of Example 4 was prepared in the same manner as in Example 1 except that the (B) filler dispersion b-1 used in Example 1 was changed to the filler dispersion b-2.

[0364] *Example 5*

A light-shielding composition of Example 5 was prepared in the same manner as in Example 1 except that the (B) filler dispersion b-1 used in Example 1 was changed to the filler dispersion b-3.

[0365] *Example 6*

A light-shielding composition of Example 6 was prepared in the same manner as in Example 1 except that the (B) filler dispersion b-1 used in Example 1 was changed to the filler dispersion b-4.

[0366] *Example 7*

A light-shielding composition of Example 7 was prepared in the same manner as in Example 1 except that the (B) filler dispersion b-1 used in Example 1 was changed to the filler dispersion b-5.

[0367] *Example 8*

A light-shielding composition of Example 8 was prepared in the same manner as in Example 1 except that the (C) filler dispersion c-1 used in Example 1 was changed to the

filler dispersion c-3.

[0368] *Example 9*

A light-shielding composition of Example 9 was prepared in the same manner as in Example 1 except that the (B) filler dispersion b-1 used in Example 1 was changed to the filler dispersion b-7.

[0369] *Example 10*

A light-shielding composition of Example 10 was prepared in the same manner as in Example 9 except that the (E) photopolymerization initiator (IRGACURE 907, trade name, manufactured by BASF Corporation, Japan) used in Example 9 was changed to a photopolymerization initiator IRGACURE 369 (trade name, manufactured by BASF Corporation, Japan).

[0370] *Example 11*

A light-shielding composition of Example 11 was prepared in the same manner as in Example 9 except that the (E) photopolymerization initiator (IRGACURE 907, trade name, manufactured by BASF Corporation, Japan) used in Example 9 was changed to a photopolymerization initiator IRGACURE 379 (trade name, manufactured by BASF Corporation, Japan).

[0371] *Example 12*

A light-shielding composition of Example 12 was prepared in the same manner as in Example 10 except that the (C) filler dispersion c-1 used in Example 10 was changed to the filler dispersion c-4.

[0372] *Example 13*

A light-shielding composition of Example 13 was prepared in the same manner as in Example 10 except that the (C) filler dispersion c-1 used in Example 10 was changed to the filler dispersion c-5.

[0373] *Example 14*

A light-shielding composition of Example 14 was prepared in the same manner as in Example 10 except that the (C) filler dispersion c-1 used in Example 10 was changed to the filler dispersion c-6.

[0374] *Comparative Example 1*

A light-shielding composition of Comparative Example 1 was prepared in the same manner as in Example 1 except that the filler dispersion c-1 used in Example 1 was not added.

[0375] *Comparative Example 2*

A light-shielding composition of Comparative Example 2 was prepared in the same manner as in Example 1 except that the filler dispersion b-1 used in Example 2 was not added.

[0376] *Comparative Example 3*

A light-shielding composition of Comparative Example 3 was prepared in the same manner as in Example 1 except that the (B) filler dispersion b-1 used in Example 1 was changed to the filler dispersion b-6.

[0377] The thus-obtained light-shielding compositions of Examples 1 to 14 each had, after the (B) first filler and the (C) second fillers were mixed, a bimodal particle diameter distribution including a maximum value within the wavelength range described for the (B) first filler and a maximum value within the wavelength range described for the (C) second filler.

The thus-obtained light-shielding compositions of Examples 1 to 14 and Comparative Examples 1 to 3 were evaluated in accordance with the following method.

[0378] *Evaluation of suitability for thick film formation*

Each light-shielding composition was applied on a silicon wafer at a rate of 900 rpm for 25 seconds by a spin coating method. Then, the resulting silicon wafer was heated on a hot plate at 120°C for 2 minutes, and a film thickness was then measured by the method described below. In a case in which the film had a thickness of 20 μm or higher, the film thickness was considered to be "tolerable".

Method for measuring a film thickness: a film thickness was measured using a Dektak 6M (trade name, manufactured by ULVAC; a contact surface-shape measuring apparatus).

[0379] *Evaluation of coating uniformity*

The coating uniformity of coated film thus obtained was evaluated by visual observation, and ranking was performed using five grades (5 to 1), based on the following evaluation criteria. The rank "3" or higher was considered to be "acceptable".

Evaluation criteria

5: No roughness is observed at the surface, and there is no problem in surface property.

4: Almost no roughness is observed at the surface, and there is almost no problem in surface property.

3: Roughness is observed in a part of the surface, and the surface property is slightly inferior, but is at a tolerable level.

2: Roughness is observed in most parts of the surface, and the surface property is inferior, which is an intolerable level.

1: Roughness is observed all over the surface, and the surface property is considerably inferior, which is an intolerable level.

[0380] *Evaluation of thickness uniformity on uneven surface*

A simulated uneven pattern was formed on a silicon wafer, and the simulated uneven pattern is formed from convex portions having a height of 20 μm with a distance between them of 50 μm . Separately, coating conditions under which a film having a thickness of 10 μm is formed on a silicon wafer having no simulated uneven pattern, were determined. Each light-shielding composition was spin-coated on a silicon wafer having the simulated uneven pattern under the above-mentioned coating conditions, followed by pre-baking at 100°C for 120 seconds and UV curing. A cross-section of the uneven portion of the substrate was photographed using a scanning electron microscope (SEM), and the thinnest thickness of the resulting film in the concave region (i.e., the region between convex portions) was measured, and thickness uniformity on uneven surface was evaluated.

The thinnest film thickness of the resulting film in the concave region was evaluated as a relative value, assuming that a desired thickness of 10 μm was 100. When the value was near 100, thickness uniformity on uneven surface was considered to be good, and when the value was 130 or higher, the value was considered to be "intolerable".

[0381] *Evaluation of high-temperature and high-humidity durability (evaluation of insulating reliability): HAST test*

Each light-shielding composition was applied on a base material in which an anode line made of copper was formed in a comb-form on a silicon wafer such that line/space of a copper material having a copper thickness of 12 μm was 50 μm /50 μm by a spin coating method such that the film thickness (film thickness after pre-baking) on copper lines was adjusted to 20 μm , and then heated on a hot plate at 100°C for 2 minutes of heating, thereby obtaining a coated film.

Then, the coated film was exposed to light at 800 mJ/cm^2 using a high-pressure mercury lamp.

After the light exposure, the coated film was subjected to paddle development using a 2.38 wt% aqueous solution of tetramethylammonium hydroxide at 25°C for 40 seconds. Then, the film was washed in a spin shower, additionally washed with pure water, and heated (post-baked) at 150°C for one hour, thereby forming a solder resist pattern (permanent pattern).

The formed permanent pattern was subjected to HAST (Highly Accelerated Stress Test) to evaluate dendrite and dielectric resistance (Ω). In the HAST, a voltage of 10 V was applied to an eclectic component module at a temperature of 130°C under an 85% relative humidity atmosphere for 200 hours and dielectric resistance (Ω) of a conductor bump was then measured under the same conditions using a high-acceleration rate tester. Then, dendrite of the conductor bump was observed and evaluated as follows. The grades of 3 or

higher were considered to be acceptable.

[0382] *Evaluation criteria*

5: No change in line was observed.

4: No dendrite was observed, but slight change in anode line was observed.

3: No dendrite was observed, but anode line was less-visible.

2: Dendrites were observed, and anode line was hard to be observed.

1: Dendrites were present.

[0383] Table 1

	(B) Filler particle diameter (nm)	(C) Filler particle diameter (nm)	Thick film formation (μm)	Coating uniformity	Thickness uniformity on uneven surface (desired value: 100)	Durability to high-temperature and high-humidity
Example 1	250	17	25	5	110	5
Example 2	250	17	24	4	115	4
Example 3	250	17	24	4	117	4
Example 4	500	17	24	4	112	4
Example 5	900	17	23	4	115	4
Example 6	1600	17	23	3	117	4
Example 7	2200	17	23	3	117	3
Example 8	250	40	23	4	121	4
Example 9	250	17	25	5	109	5
Example 10	250	17	25	5	106	5
Example 11	250	17	25	5	107	5
Example 12	250	17	25	5	105	5
Example 13	250	17	24	5	105	5
Example 14	250	17	25	5	104	5
Comparative Example 1	250	-	15	15	150	2
Comparative Example 2	-	17	19	19	135	2
Comparative Example 3	4000	17	23	23	135	2

[0384] As shown in Table 1, in Examples 1 to 8 in which the light-shielding compositions of the present invention were used, films which exhibit a superior suitability for thick film formation and have film thicknesses of 20 μm or more were obtained, an excellent coating uniformity and an excellent thickness uniformity on uneven surface were obtained, and the films had excellent durability to high-temperature and high-humidity. By comparing Example 1 and Example 8, it was found that, when the (B) fillers having the same particle diameter were used, use of a (C) filler having a relatively smaller particle diameter achieved superior effects in terms of suitability for thick film formation, thickness uniformity on uneven surface, coating uniformity and durability to high-temperature and high-humidity.

In contrast, in Comparative Examples 1 and 2 in which the light-shielding composition of the present invention, thick layers were not able to be formed, and thickness uniformity on uneven surface and durability to high-temperature and high-humidity were inferior. In Comparative Example 3, a relatively thicker layer was able to be formed, but durability to high-temperature and high-humidity was inferior.

[0385] Japanese Patent Application Nos. 2011-040505 and 2011-102134 are incorporated herein by reference.

All publications, patent applications, and technical standards mentioned in this specification are herein incorporated by reference to the same extent as if each individual publication, patent application, or technical standard was specifically and individually indicated to be incorporated by reference.

Claim 1. A light-shielding composition, comprising:

(A) any one of a light-shielding particle or a light-shielding dye;

(B) a first filler having a particle diameter of from 100 nm to 3,000 nm, the particle diameter being a maximum value in a particle diameter distribution of the first filler; and

(C) a second filler having a particle diameter of from 5 nm to 90 nm, the particle diameter being a maximum value in a particle diameter distribution of the second filler,

wherein, when the (B) first filler and the (C) second filler are mixed in the light-shielding composition, the particle diameter distribution among the mixed fillers includes a maximum value within a range from 5 nm to 90 nm and a maximum value within a range from 100 nm to 3,000 nm.

Claim 2. The light-shielding composition according to claim 1, wherein the light-shielding particle comprises a pigment.

Claim 3. The light-shielding composition according to claim 1 or 2, wherein the light-shielding particle comprises an inorganic pigment.

Claim 4. The light-shielding composition according to any one of claims 1 to 3, wherein the particle diameter of the light-shielding particle is from 5 nm to 100 nm, the particle diameter being a maximum value in a particle diameter distribution of the light-shielding particle.

Claim 5. The light-shielding composition according to any one of claims 1 to 4, wherein the light-shielding particle comprises at least one selected from the group consisting of titanium black, carbon black, and cesium tungsten oxide.

Claim 6. The light-shielding composition according to any one of claims 1 to 5, wherein at least one of the (B) first filler or the (C) second filler comprises an inorganic filler.

Claim 7. The light-shielding composition according to any one of claims 1 to 6, wherein at least one of the (B) first filler or the (C) second filler comprises silica.

Claim 8. The light-shielding composition according to any one of claims 1 to 7,

wherein at least one of the (B) first filler or the (C) second filler has a substantially spherical shape.

Claim 9. The light-shielding composition according to any one of claims 1 to 8, wherein a ratio of contents of the (B) first filler and the (C) second filler is from 1:30 to 1:2 in mass basis.

Claim 10. The light-shielding composition according to any one of claims 1 to 9, further comprising:

(D) a polymerizable compound; and

(E) a photopolymerization initiator.

Claim 11. A method of producing the light-shielding composition according to any one of claims 1 to 10, comprising:

mixing a dispersion comprising the light-shielding particle, a dispersion comprising the (B) first filler, and a dispersion comprising the (C) second filler, which are prepared as separate dispersions.

Claim 12. A solder resist, comprising the light-shielding composition according to any one of claims 1 to 10.

Claim 13. A method of producing a pattern, comprising:

forming a photosensitive layer using the solder resist according to claim 12 on a substrate;

subjecting the photosensitive layer to pattern light exposure to cure an exposed region thereof; and

subjecting the photosensitive layer after the pattern light exposure to alkali development.

Claim 14. A solid-state imaging device, comprising a solder resist layer formed using the solder resist according to claim 12.

FIG.1

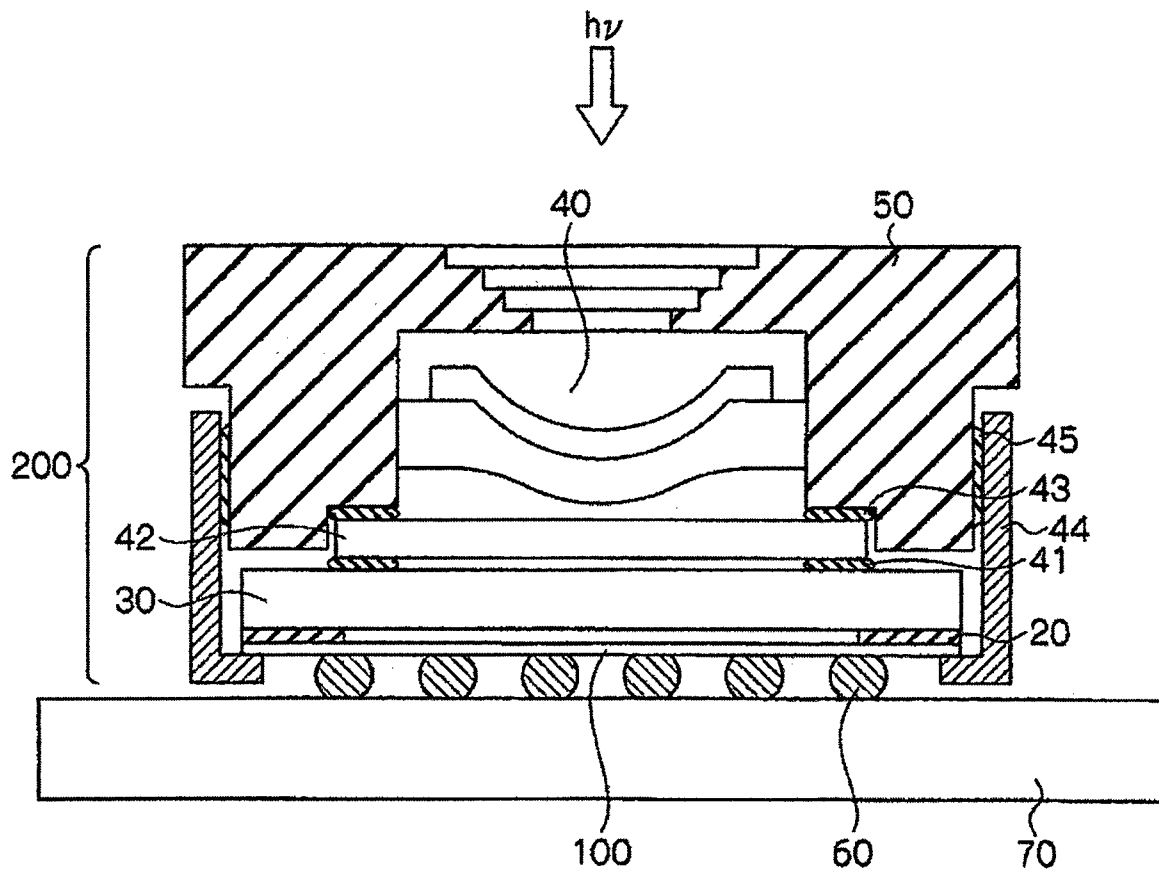
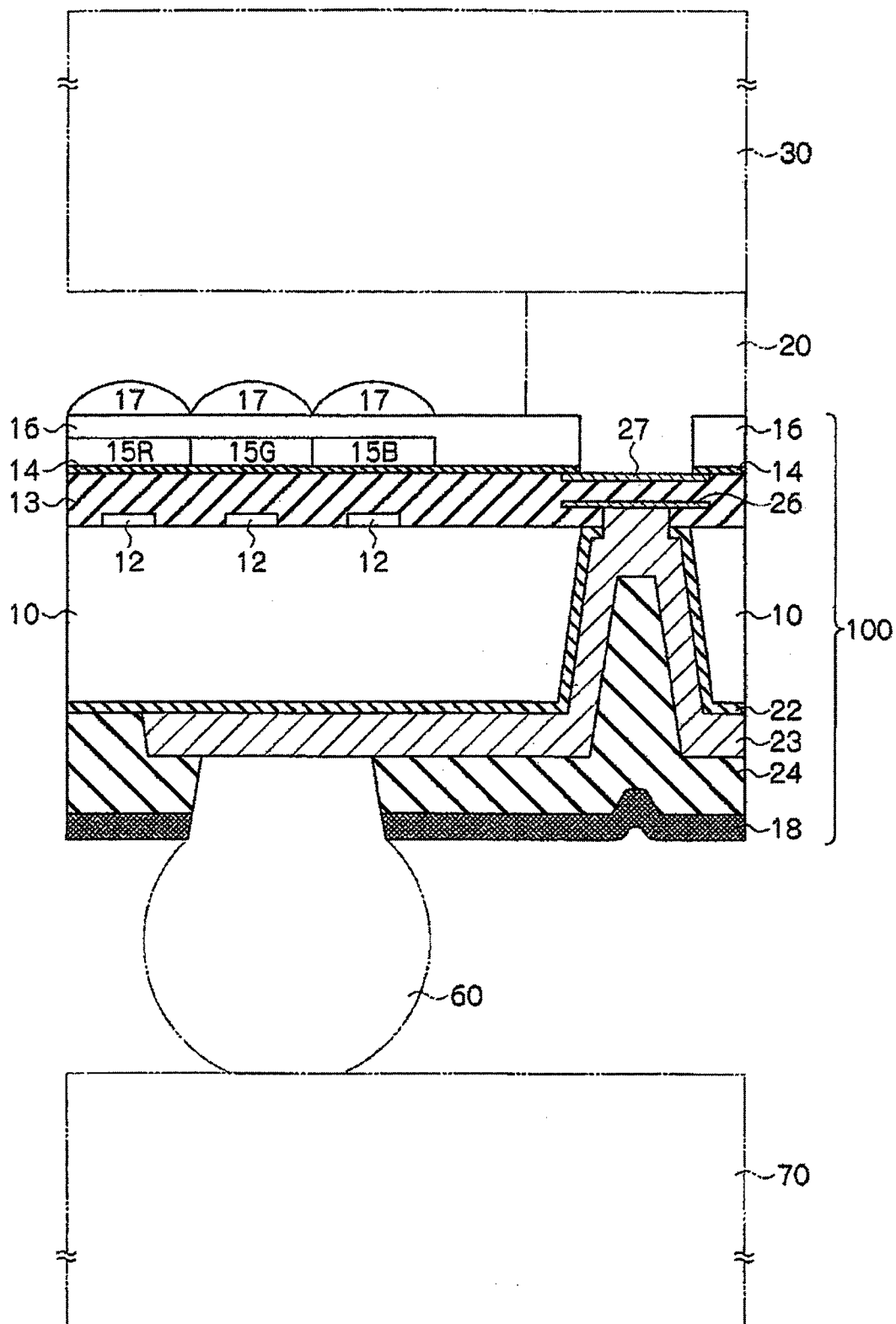


FIG.2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/054672

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. G02B5/22 (2006.01) i, G03F7/004 (2006.01) i, H01L27/14 (2006.01) i,
H05K3/28 (2006.01) i

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)

Int.Cl. G02B5/20-5/28, G02B 5/00-5/136, H01J 11/00-17/64, B29D 9/00, B32B 1/00-35/00,
G03F7/004, H01L27/14, H05K3/28

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2012
Registered utility model specifications of Japan 1996-2012
Published registered utility model applications of Japan 1994-2012

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2009-288756 A (TOYO BOSEKI KABUSHIKIKAI) 2009.12.10 , paragraphs 【0002】 , 【0093】 , 【0094】 (No family)	1-14
A	JP 2010-134002 A (TORAY ADVANCED FILM CO., LTD.) 2010.06.17, paragraph 【0013】 (No family)	1-14
A	JP 2008-284741 A (RIKEN TECHNOS CORP.), 2008.11.27, paragraph 【0007】 (No family)	1-14

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

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“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

17.04.2012

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/054672

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2008-216568 A (Sumitomo Osaka Cement Co., Ltd.) 2008.09.18, paragraph 【0009】 (No family)	1-14
A	JP 2007-140098 A (TEIJIN DUPONT FILMS JAPAN LIMITED) 2007.06.07, paragraph 【0032】 (No family)	1-14
A	JP 2009-99591 A (KABUSHIKI KAISHA TOSHIBA) 2009.05.07, Fig. 16 & US 2009/0096051 A1	12-14