

DESCRIPTION

BLACK POLYMERIZABLE COMPOSITION AND METHOD FOR PRODUCING A
BLACK LAYER

TECHNICAL FIELD

[0001] The present invention relates to a black polymerizable composition including a specific alkali-soluble binder polymer, in particular, a black polymerizable composition used for forming a light-shielding region of a wafer level lens array, in which plural lenses are arranged on a substrate, and a method for producing a black layer using the black polymerizable composition.

BACKGROUND ART

[0002] Recently, compact and low-profile (thin) imaging units have been mounted on mobile terminals of electronic instruments such as mobile phones or Personal Digital Assistants (PDAs). These imaging units generally include solid-state imaging devices such as an image sensor of a Charge Coupled Device (CCD) type or an image sensor of a Complementary Metal-Oxide Semiconductor (CMOS) type, and a lens for forming a subject image on the solid-state imaging devices.

[0003] With the reduction in size and thickness of the mobile terminals and with the widespread use of the mobile terminals, further reduction in the size and thickness of an imaging unit mounted on the mobile terminals is required and improvement in the productivity thereof is also required. With respect to such requirements, a method of mass-producing imaging units is known whereby a lens substrate having plural lenses formed thereon and a sensor substrate having plural solid-state imaging devices formed thereon are integrally combined, and the lens substrate and the sensor substrate are cut so as to include a lens and a solid-state imaging device in each cut portion.

In addition, adopting a method of forming a lens on a wafer enables various simple methods of formation to be carried out including, for example, a method where only lenses are produced on a glass wafer, for example, which is cut to a size for combination of the respective lenses with sensors, followed by combination with pre-separated imaging devices to produce respective imaging units; a method where plural lenses are formed from only a resin using a mold, which are combined on a sensor substrate and then cut; and a method where a lens is cut to a size for combination with respective sensors, followed by combination with pre-separated imaging devices, to produce respective imaging units.

Hereinbelow, in the present specification, each one of plural lenses formed on a lens substrate is referred to as a wafer level lens, and a group of lenses formed on a lens substrate, including the lens substrate, is referred to as a wafer level lens array.

[0004] As a wafer level lens array in the related art, a wafer level lens array is known that has plural lenses formed thereon by applying dropwise a curable resin material onto the surface of a parallel plate (substrate) formed of a light transmissive material such as glass and curing the resin material in a state in which it is arranged in a prescribed shape using a mold (for example, see Japanese Patent Publication No. 3926380 and International Application Publication No. WO 2008/102648). In some cases, a light-shielding section formed, for example, from a black film or a metal film may be formed in a region other than a lens portion of a wafer level lens or on a part of the lens in order to control the amount of light passing therethrough. The light-shielding section is generally formed by coating a light-shielding curable composition or by depositing metals.

[0005] As another wafer level lens array, a wafer level lens array is also known that is obtained by forming plural through-holes on a silicon substrate, disposing spherical lens materials, which have been separately-formed, in the respective through-holes, bonding the lens materials to the substrate by soldering, and then polishing the lens materials to form plural lenses (see US Patent No. 6426829). In a lens obtained by this production method, the black film or the metal film described above may be formed in order to control the amount of light passing therethrough.

[0006] In a case in which a light-shielding region is formed by deposition of a metal, an improvement is required in terms of both of productivity and performance, from the viewpoints that there are problems such as complicated processes or lens bending after deposition.

[0007] On the other hand, a black polymerizable composition has been used in a coating method in order to exhibit a light-shielding property (see Japanese Patent Application Laid-Open (JP-A) Nos. 2010-8656 and 2006-276421).

In a case in which a black polymerizable composition has a sufficient light-shielding property in a visible region, the transmittance of a radiation selected from g-rays, h-rays, i-rays, and/or the like, which are exposure light sources used for curing the black polymerizable composition, is not sufficient. For this reason, the film is not sufficiently cured in a deep portion, and therefore, after image-wise exposure, there have been problems such as peeling in the film in an alkali development step in which an unexposed portion is to be removed.

[0008] Thus, an investigation regarding such problems concerning alkali developer resistance has not been sufficiently carried out yet.

SUMMARY OF INVENTION

[0009] The present invention is made in view of above-mentioned aspects, and is directed to approach the objects as described below.

That is, an aspect of the invention is to provide a black polymerizable composition that has alkali developer resistance, and accordingly, has an excellent light-shielding property.

It is another aspect of the invention to provide a black polymerizable composition capable of being spray-coated.

It is still another aspect of the invention to provide a method for producing a black layer, which is useful for a light-shielding region of a wafer level lens, using the black polymerizable composition.

[0010] Generally, a resin containing a carboxylic acid as an alkali-soluble group is used in a curable composition. However, in a case in which development is carried out under relatively severe conditions so as to remove the residue of an unexposed portion, there have been problems such as peeling of an image portion.

Meanwhile, in a case of using the curable composition for an aperture of a lens, a light-shielding property widely ranging from a visible region to an infrared region is required.

In a case in which a light-shielding film is formed using a black polymerizable composition, image-wise exposure is carried out generally with a light source of from 250 nm to 500 nm, followed by development using an alkali developer. However, since the curable composition includes a black material capable of shielding light at a wavelength region of from 250 nm to 500 nm, the light transmittance of the exposure light source is insufficient, and thus, a deep portion of the formed film may not be sufficiently cured in some cases. Therefore, in a case in which development is carried out under relatively severe conditions in order to prevent reduction of the residual film, a strongly acidic carboxylic acid may cause penetration of the developer into the image portion, and thus, there has been a concern that reduction of the strength of the image portion may lead to peeling of the light-shielding film (black film).

Furthermore, in a case in which the black polymerizable composition (or the curable composition) is used for an aperture or the like of a wafer level lens, a method in which a black polymerizable composition is coated on a glass wafer and then a lens is formed thereon, a method in which a lens is formed on a glass wafer and then a black polymerizable composition is coated thereto, or the like may be employed. However, particularly in the case in which a black polymerizable composition is coated after a lens has been formed, it is effective to apply the black polymerizable composition on the structure substrate by spray

coating.

In other words, the inventors of the present invention have extensively studied various black polymerizable compositions, and as a result, have found a black polymerizable composition having alkali developer resistance, and accordingly, having an excellent light-shielding property. The inventors have also found a black polymerizable composition capable of being spray-coated. In addition, the inventors have found a method for producing a black layer, which is useful in a light-shielding region of a wafer level lens, using the black polymerizable composition.

Specific exemplary embodiments of the invention are as follows.

<1> A black polymerizable composition, including:

(A) a black material;

(B) a polymerization initiator;

(C) a polymerizable compound; and

(D) an alkali-soluble binder polymer having a weight average molecular weight of at least 30,000 and having a polymerizable group at a side chain thereof.

<2> The black polymerizable composition according to <1>, wherein the (A) black material is titanium black.

<3> The black polymerizable composition according to <1> or <2>, wherein the (D) alkali-soluble binder polymer is an alkali-soluble binder polymer having a weight average molecular weight of from 50,000 to 100,000 and having a polymerizable group at a side chain thereof.

<4> The black polymerizable composition according to any one of <1> to <3>, which is used for forming a light-shielding region of a wafer level lens.

<5> The black polymerizable composition according to any one of <1> to <4>, which is capable of being spray-coated.

<6> The black polymerizable composition according to any one of <1> to <5>, wherein the total solid content in the black polymerizable composition is from 20% by mass to 35% by mass.

<7> The black polymerizable composition according to any one of <1> to <6>, wherein the polymerizable group included in the (D) alkali-soluble binder polymer is an acryl group, a methacryl group, a styryl group, an allyl group, an acrylamide group, a methacrylamide group, a vinyl group or a vinyl ether group.

<8> The black polymerizable composition according to any one of <1> to <7>, wherein a content of the (D) alkali-soluble binder polymer is from 5% by mass to 75% by mass with respect to the total solid content of the black polymerizable composition.

<9> A method for producing a black layer, the method including:

applying, by spray coating, the black polymerizable composition according to any one of <1> to <8> onto a surface of a solid to form a black polymerizable composition layer; and

applying energy to the formed black polymerizable composition layer to cure the formed black polymerizable composition layer.

<10> The method for producing a black layer according to <9>, wherein the surface of the solid is a surface of a peripheral portion of a wafer level lens, and the black layer is a light-shielding region formed in the peripheral portion of a wafer level lens.

[0011] According an aspect of the invention, a black polymerizable composition that has an alkali developer resistance, and accordingly, exhibits an excellent light-shielding property is provided.

Further, according to another aspect of the invention, a black polymerizable composition capable of being spray-coated is provided.

In addition, according to still another aspect of the invention, a method for producing a black layer which is useful for a light-shielding region of a wafer level lens, is provided using the black polymerizable composition.

BRIEF DESCRIPTION OF DRAWINGS

[0012] Fig. 1 is a plain view showing an example of a wafer level lens array.

Fig. 2 is a cross-sectional view of the wafer level lens array shown in Fig. 1, which is taken along the line A-A.

Fig. 3 is a view showing the state of supplying a molding material for forming a lens onto a substrate.

Figs. 4A to 4C are views showing the process of forming lenses on a substrate using a mold.

Figs. 5A to 5C are schematic views showing the process of forming a patterned light-shielding film on the substrate having the lenses formed thereon.

Fig. 6 is a view showing an example of a wafer level lens array.

Figs. 7A to 7C are schematic views showing another embodiment of the process of forming a light-shielding film.

Figs. 8A to 8C are schematic views showing the process of forming lenses on a substrate having a patterned light-shielding film.

DESCRIPTION OF EMBODIMENTS

[0013] Hereinbelow, the black polymerizable composition of the invention will be described in detail. Explanation of the constituent elements described below is made on the basis of the representative embodiments of the invention, but the invention is not limited to such embodiments.

In the specification, the term “step” or “process” is not only an independent step, but also includes a case of attaining a predetermined action of the step even when it cannot be clearly discriminated from other steps.

Further, in the specification, the numerical range expressed by using “to” denotes a range including a minimal value and a maximal value described before and after the “to”.

[0014] *(D) Alkali-Soluble Binder Polymer*

The black polymerizable composition of the invention includes an alkali-soluble binder polymer having a weight average molecular weight of 30,000 and having a polymerizable group at a side chain thereof.

Examples of the polymer that constitutes the main chain of the (D) alkali-soluble binder polymer used in the invention include (meth)acrylic polymers, polyurethane resins, polyvinyl alcohol resins, polyvinyl butyral resins, polyvinyl formal resins, styrene resins, polyamide resins, polyester resins, epoxy resins, and phenolic resins such as a novolak resin or a resol resin. Particularly, (meth)acrylic polymers, styrene resins, and phenolic resins are preferable. Further, from the viewpoints of sensitivity and resolution, (meth)acrylic polymers and polyurethane resins are preferable, and (meth)acrylic polymers are most preferable.

[0015] The “(meth)acrylic polymer(s)” in the invention refers to a copolymer having, as a polymerization component, a (meth)acrylic acid, a (meth)acrylic ester (such as an alkyl ester, an aryl ester, an allyl ester, or the like), a (meth)acrylamide, or a (meth)acrylic acid derivative such as a (meth)acrylamide derivative.

In the specification, in the case in which either or both of “acryl” and “methacryl” is described, “(meth)acryl” may be denoted in some cases.

The “polyurethane resin” in the invention refers to a polymer produced by a condensation reaction of a compound having two or more isocyanate groups and a compound having two or more hydroxyl groups.

The “polyvinyl butyral resin” in the invention refers to a polymer synthesized by subjecting a polyvinyl alcohol obtained by a saponification of a part or whole of polyvinyl acetate to a reaction (acetal-forming reaction) with butyl aldehyde under an acidic condition, as well as a polymer having an acid group or the like introduced therein by, for example, a method involving reacting the remaining hydroxyl group with a compound having an acid

group or the like.

[0016] The “styrene resin” in the invention refers to a polymer obtained by copolymerization (e.g., radical polymerization) of an aromatic compound such as benzene, naphthalene, anthracene, or a heterocycle, to which an alkenyl group such as a vinyl group is directly linked, and (meth)acrylic acid and/or a (meth)acrylic acid derivative.

The aromatic compound may be substituted with, for example, a hydroxyl group, a carboxylic group, a halogen atom, an alkyl group, an alkenyl group, an alkynyl group, an amino group, a carbonyl group, an ether group, an alkoxy carbonyl group, an oxycarbonyl group, a cyano group, an aryl group, an alkoxy group, a sulfide group, a mercapto group, or the like.

As for the polymerization, it is possible to carry out radical polymerization, cation polymerization, or anion polymerization. Furthermore, after the polymerization, if necessary, an alkali treatment, an acid treatment, or the like may be carried out to obtain a desired styrene resin.

[0017] Any one of other resins may be used for the polymer constituting the main chain of the alkali-soluble binder polymer in the invention. For example, the polyurethane resins described in paragraphs [0029] to [0108] of JP-A No. 2005-250438 and the like, a resin having an amide and a polymerizable group in a molecule thereof described in paragraphs [0009] to [0019] of JP-A No. 2010-39121 and the like, and a resin obtained by reacting a resin having, as a main component, acrylic acid and a (meth)acrylic ester with an epoxy group-containing unsaturated compound described in paragraphs [0014] to [0015] of JP-A No. 2000-191737 and the like, may be used.

[0018] The alkali-soluble binder polymer in the invention preferably has a high molecular weight is preferable in terms of inhibiting elution of an image portion that is an exposed portion into a developer during development, and has a polymerizable group in order to improve the curability.

The weight average molecular weight of the alkali-soluble binder polymer in the invention is at least 30,000. When the weight average molecular weight is less than 30,000, resistance of the image portion to the developer is not sufficient.

Furthermore, from the viewpoint of the developability of the image portion and non-image portion, the weight average molecular weight of the alkali-soluble binder polymer is preferably from 30,000 to 500,000, more preferably from 40,000 to 200,000, and even more preferably from 50,000 to 100,000.

In the invention, the weight average molecular weight refers to a value measured in terms of styrene by means of a Gel Permeation Chromatography (GPC) method.

[0019] The alkali-soluble binder polymer in the invention has a polymerizable group at a side chain of the polymer. Examples of the polymerizable group included in the side chain include an acryl group, a methacryl group, a styryl group, an allyl group, an acrylamide group, a methacrylamide group, a vinyl group, and a vinyl ether group. From the viewpoints of stability and reactivity, an acryl group, a methacryl group, and an allyl group are preferable, and a methacryl group is most preferable.

The amount of the polymerizable group included in the side chain is preferably from 10% by mole to 80% by mole, in the total monomer units each having a polymerizable group in the polymers, and from the viewpoints of sensitivity, developability, and stability, it is more preferably from 30% by mole to 60% by mole.

[0020] Here, examples of the method for introducing a polymerizable group into the alkali-soluble binder polymer include a method in which a part of carboxylic acids in the binder is reacted with a compound having a cyclic ether and a (meth)acryl group, such as glycidyl methacrylate, so as to introduce the polymerizable group, as described in paragraph [0014] of JP-A No. 2000-187322 and the like; a method in which a resin having acrylic acid and a (meth)acrylic ester as main components is reacted with an epoxy group-containing unsaturated compound, and a binder in which a monomer having a hydroxyl group is used as a copolymerization component is reacted with a methacrylic anhydride or acrylic anhydride, or acrylic chloride or methacrylic chloride, as described in JP-A No. 2000-191737; or a method in which a binder in which a monomer having a hydroxyl group is used as a copolymerization component is allowed to coexist with methacrylic acid or acrylic acid, and subjected to dehydration/condensation, and a method in which a monomer having methacrylic acid derivative and/or an acrylic acid derivative at a side chain is polymerized and subjected to a treatment with a base, as described in paragraph [0028] of JP-A No. 2005-47947 and the like.

[0021] The alkali-soluble binder polymer in the invention has a functional group that expresses alkali solubility. As the functional group that imparts alkali solubility to the binder polymer, it is necessary that the binder polymer has an acid group a molecule thereof. Examples of preferable acid groups include a carboxylic acid group, a phosphoric acid group, a monophosphoric ester group, a sulfonic acid group, a sulfinic acid group, a sulfonamide group, a phenolic hydroxyl group, a thiol group, an alkyl acetyl acetate group, and derivatives thereof.

From the viewpoints of sensitivity, stability, and developability, the acid group is preferably a carboxylic acid group.

When the alkali-soluble binder polymer in the invention has an alkali-soluble group,

the acid value is preferably 5 mgKOH/g to 150 mgKOH/g, and most preferably 30 mgKOH/g to 100 mgKOH/g.

As for a method for introducing the functional group that imparts alkali solubility to the binder polymer, when polymerization is performed by radical polymerization, the functional group that imparts alkali solubility to the binder polymer may be introduced by polymerization of a compound having an acid group and a polymerizable group such as an ethylene group, such as methacrylic acid, acrylic acid, vinylbenzoic acid, or vinylphenol. Further, introduction of the functional group may also be achieved by polymerizing acetoxystyrene, followed by hydrolysis.

In a case of a urethane binder, for example, a method in which a diol having a carboxylic acid moiety and a diisocyanate compound are subjected to a polycondensation reaction to introduce an acid group may be employed.

[0022] When a polymer that constitutes the main chain of the alkali-soluble binder polymer in the invention is a (meth)acrylic polymer, a polymer having a carboxylic acid group may be obtained by radical polymerization.

Examples of the acid group-containing monomer that may be used in the radical polymerization include acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, phthalic acid monohydroxyethyl acrylate, ω -carboxy-polycaprolactone monoacrylate, β -carboxyethyl acrylate, 2-acryloyloxyethyl succinic acid, 2-acryloyloxyethyl hexahydrophthalate, phthalic acid monohydroxyethyl methacrylate, ω -carboxy-polycaprolactone monomethacrylate, β -carboxyethyl methacrylate, 2-methacryloyloxyethyl succinic acid, 2-methacryloyloxyethyl hexahydrophthalic acid, and 4-carboxystyrene, and examples of the monomer having an acid anhydride include anhydrous maleic acid. Further, other usable monomers may be used.

Examples of a monomer capable of being copolymerized with the acid group-containing monomer include (1) to (12) described below:

[0023] (1) Acrylic esters and methacrylic esters, each having an aliphatic hydroxyl group, such as 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 3-hydroxypropyl acrylate, 4-hydroxybutyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl methacrylate, or 4-hydroxybutyl methacrylate;

[0024] (2) Alkyl acrylates such as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, isobutyl acrylate, amyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, octyl acrylate, benzyl acrylate, 2-chloroethyl acrylate, glycidyl acrylate, 3,4-epoxycyclohexylmethyl acrylate, vinyl acrylate, 2-phenyl vinyl acrylate, 1-propenyl acrylate, allyl acrylate, 2-allyloxyethyl acrylate, or propargyl acrylate;

[0025] (3) Alkyl methacrylates such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, isobutyl methacrylate, amyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, 2-chloroethyl methacrylate, glycidyl methacrylate, 3,4-epoxycyclohexyl methyl methacrylate, vinyl methacrylate, 2-phenyl vinyl methacrylate, 1-propenyl methacrylate, allyl methacrylate, 2-allyloxyethyl methacrylate, or propargyl methacrylate;

(4) Acrylamides or methacrylamides such as acrylamide, methacrylamide, N-methylolacrylamide, N-ethyl acrylamide, N-hexyl methacrylamide, N-cyclohexyl acrylamide, N-hydroxyethyl acrylamide, N-phenyl acrylamide, N-nitrophenyl acrylamide, N-ethyl-N-phenyl acrylamide, vinyl acrylamide, vinyl methacrylamide, N,N-diallyl acrylamide, N,N-diallyl methacrylamide, allyl acrylamide, or allyl methacrylamide;

[0026] (5) Vinyl ethers such as ethyl vinyl ether, 2-chloroethyl vinyl ether, hydroxyethyl vinyl ether, propyl vinyl ether, butyl vinyl ether, octyl vinyl ether, or phenyl vinyl ether;

(6) Vinyl esters such as vinyl acetate, vinyl chloroacetate, vinyl butyrate, or vinyl benzoate;

(7) Styrenes such as styrene, α -methylstyrene, methylstyrene, chloromethylstyrene, or p-acetoxystyrene;

(8) Vinyl ketones such as methyl vinyl ketone, ethyl vinyl ketone, propyl vinyl ketone, or phenyl vinyl ketone;

(9) Olefins such as ethylene, propylene, isobutylene, butadiene, or isoprene;

[0027] (10) N-vinylpyrrolidone, acrylonitrile, methacrylonitrile, and the like;

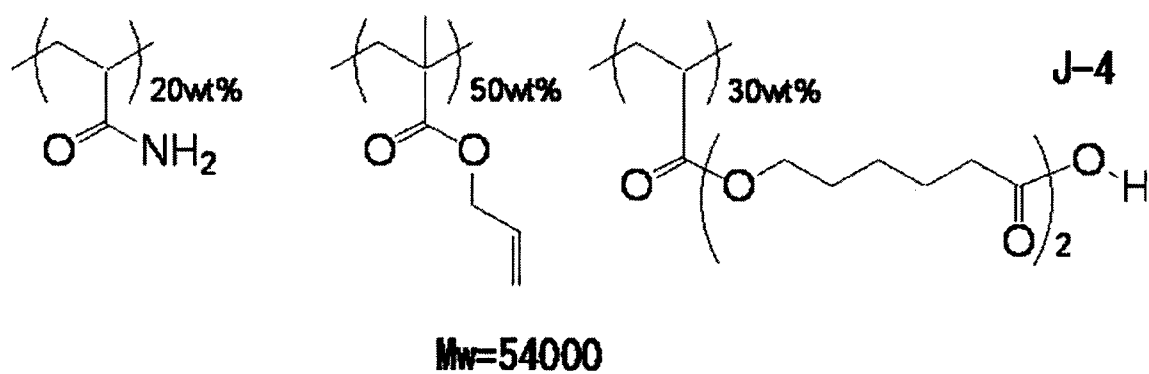
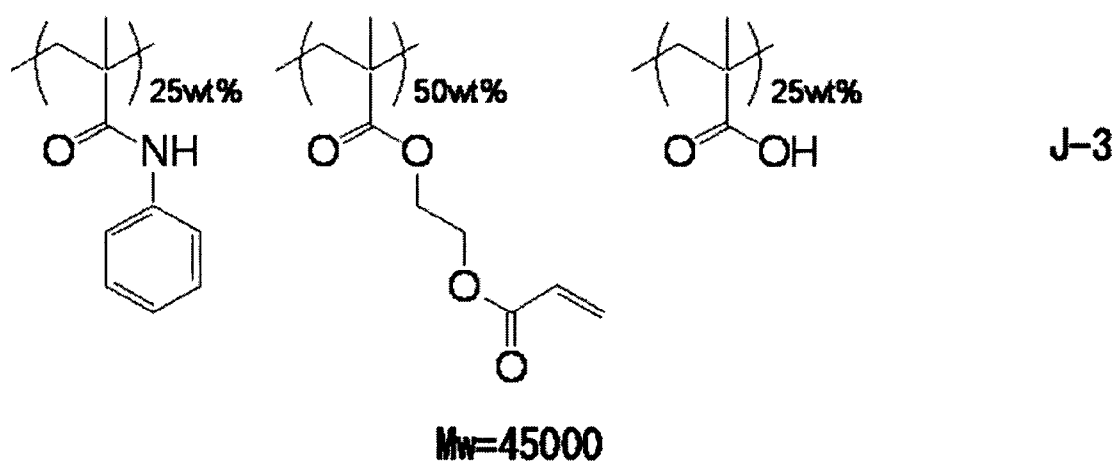
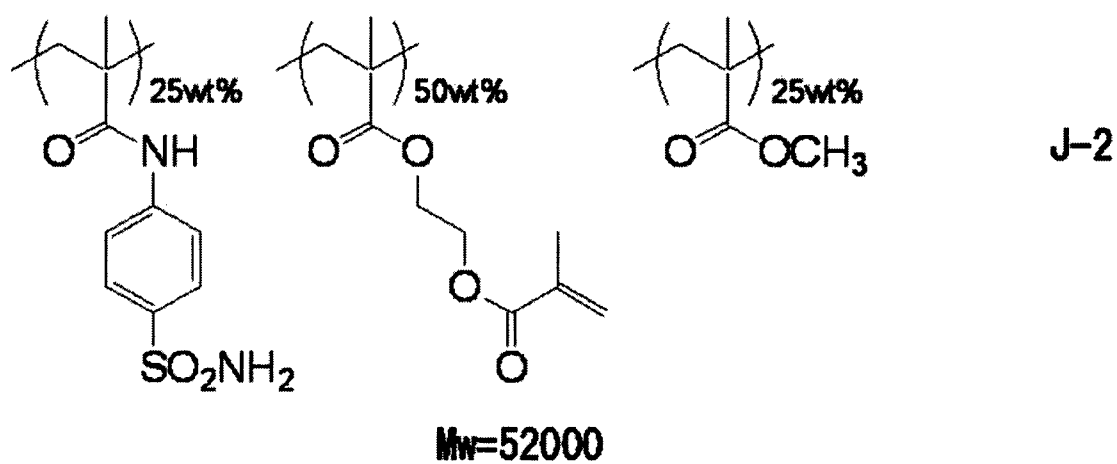
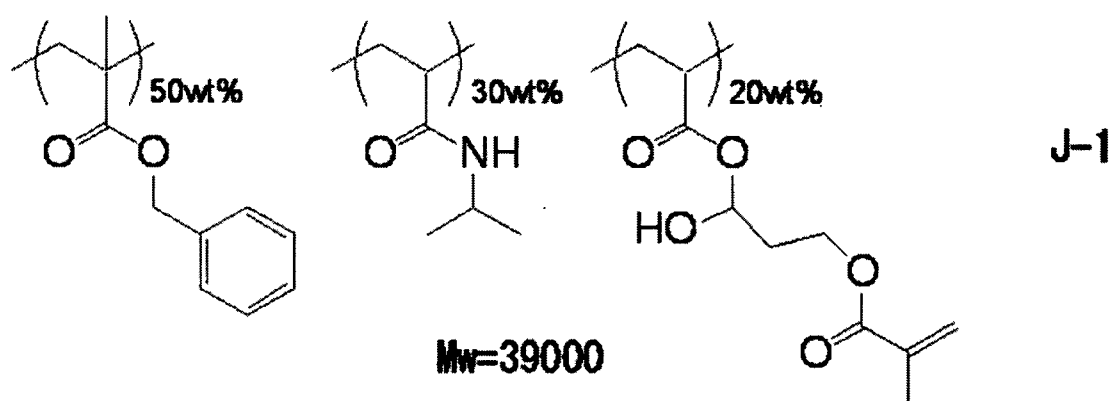
(11) Unsaturated imides such as maleimide, N-acryloyl acrylamide, N-acetyl methacrylamide, N-propionyl methacrylamide, or N-(p-chlorobenzoyl) methacrylamide; and

(12) Methacrylic acid monomers, each having a hetero atom bonded at the α -position thereof, such as the compounds described in JP-A Nos. 2002-309057 and 2002-311569, and the like.

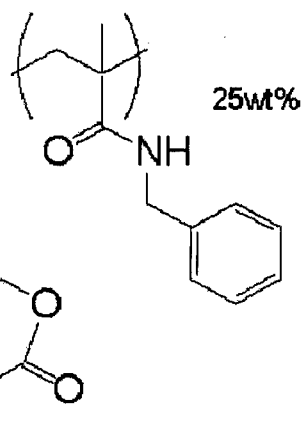
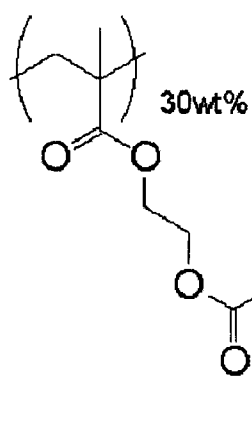
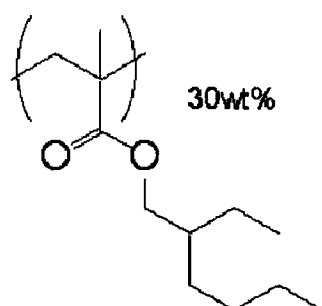
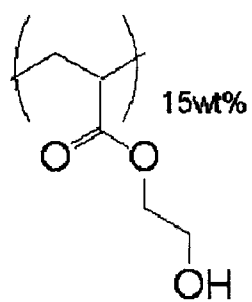
[0028] Other suitable examples thereof include (meth)acrylic polymers, each having an allyl group or a vinyl ester group and a carboxyl group at side chains thereof, and alkali-soluble resins each having a double bond at a side chain, as described in JP-A No. 2000-187322, and alkali-soluble resins, each having an amide group at a side chain, as described in JP-A No. 2001-242612.

Most preferable examples of the alkali-soluble binder polymer are shown below.

[0029]

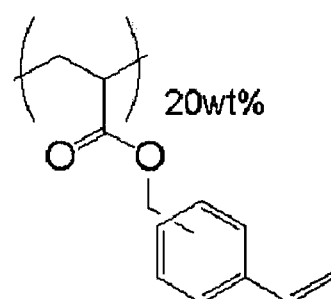
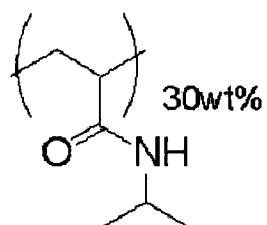
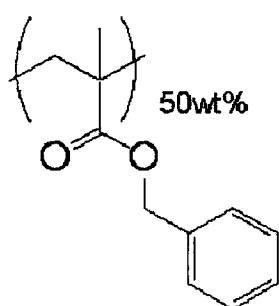


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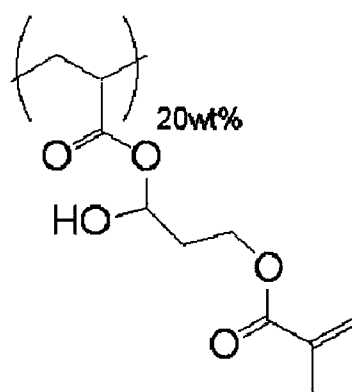
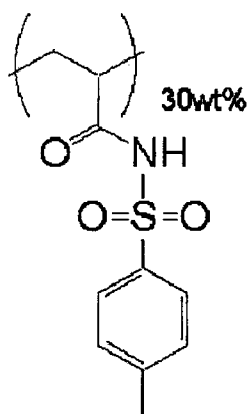
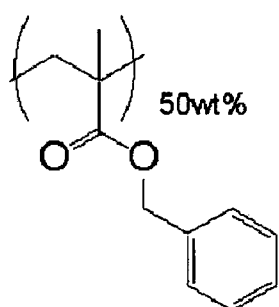
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J-6

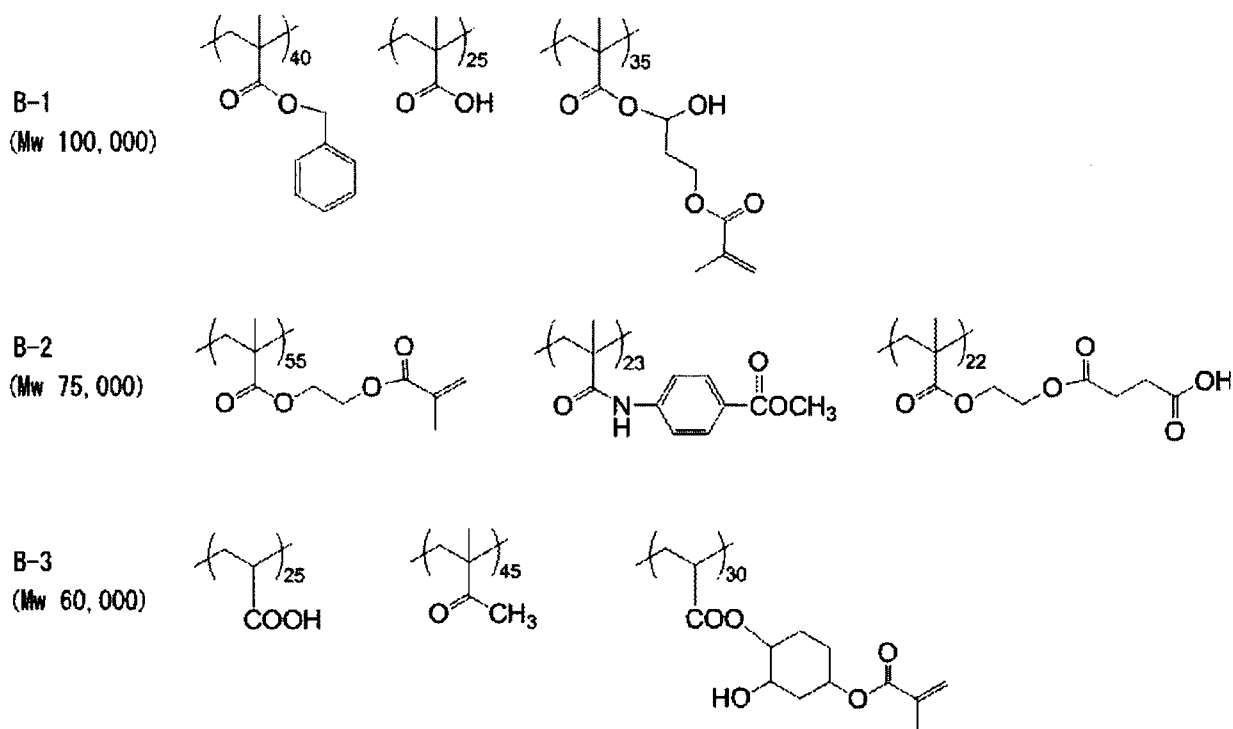
Mw=31000



J-7

Mw=37000

[0031]



[0032] In the invention, the alkali-soluble binder polymers may be used singly, or in combination of two or more kinds thereof.

The content of the alkali-soluble binder polymer is preferably from 5% by mass to 75% by mass, more preferably from 10% by mass to 70% by mass, and even more preferably from 10% by mass to 60% by mass, with respect to the total solid content of the black polymerizable composition, from the viewpoints of good intensity of an image portion and goof anti-developer resistance.

The “total solid content” as used in the invention refers to a total amount of the components of the black polymerizable composition, except for the solvent.

[0033] (A) *Black Material*

The black polymerizable composition of the invention includes a black material.

Examples of the (A) black material used in the invention include combinations of a black pigment, a black dye, a red pigment, a blue pigment, a green pigment, a yellow pigment, an orange pigment, a violet pigment, a cyan pigment, a magenta pigment, a gray pigment, and the like, or combinations of a red dye, a blue dye, a green dye, a yellow dye, an orange dye, a violet dye, a cyan dye, a magenta dye, a gray dye, and the like. From the viewpoints of a light-shielding property, storage stability, safety, and the like, a black pigment is preferably used.

Examples of the black pigment include inorganic pigments such as titanium black or carbon black.

Examples of a commercially-available product of carbon black (C. I. Pigment Black 7) include carbon black MA-100 R (trade name, manufactured by Mitsubishi Chemical Corporation).

Specific examples of the inorganic pigment other than carbon black include metal pigments, titanium black, Chinese white, lead white, lithopone, titanium oxide, chromium oxide, iron oxide, precipitated barium sulfate and baryte powder, red lead, iron oxide red, chrome yellow, zinc chromate (such as zinc potassium chromate, and zinc tetroxy chromate), ultramarine blue, Prussian blue (potassium ferric ferrocyanide), zircon gray, praseodymium yellow, chrome titanium yellow, chrome green, peacock, Victoria green, iron blue (having no relation with Prussian blue), vanadium zirconium blue, chrome tin pink, manganese pink, and salmon pink.

Examples of black inorganic pigments include a metal oxide and metal nitride containing one or two or more kinds of metal elements selected from the group consisting of Co, Cr, Cu, Mn, Ru, Fe, Ni, Sn, Ti, and Ag. These pigments may be used alone or in a mixture of two or more kinds.

In particular, these pigments may be used not only alone but also in a mixture of plural kinds of pigments, in order to express a light-shielding property in a wide wavelength region from ultraviolet to infrared light.

[0034] From the viewpoints of light-shielding property and curing property, a metal pigment and titanium black are preferable.

The metal pigment is preferably a metal pigment containing at least one of silver, tin, and the like, or a mixture of silver and tin.

From the viewpoints of a light-shielding property in a range from ultraviolet to infrared light, titanium black is most preferred.

[0035] The titanium black used in the invention is a black particle having a titanium atom. Preferable examples thereof include low order titanium oxide and titanium oxynitride.

A titanium black particle may be used as it is, or the surface thereof may be optionally modified from the viewpoints of, for example, improvement of dispersibility and suppression of aggregating property. The titanium black particle may be coated with silicon oxide, titanium oxide, germanium oxide, aluminum oxide, magnesium oxide, or zirconium oxide. Alternatively, the titanium black particle may be treated with a water repellent material as described in Japanese Patent Application Laid-Open (JP-A) No. 2007-302836.

Further, the titanium black may contain one or a combination of two or more kinds of a composite oxide of Cu, Fe, Mn, V, Ni, and the like and a black pigment such as cobalt oxide, iron oxide, carbon black, or aniline black, in order to adjust dispersibility and colorability. In

this case, the titanium black particle accounts for 50% by mass or more in the (A) inorganic pigment.

[0036] Examples of the commercially-available product of titanium black include titanium black 10S, 12S, 13R, 13M, 13M-C, 13R and 13R-N (trade names, manufactured by Mitsubishi Material Corporation) and TILACK D (trade name, manufactured by Ako Kasei Co., Ltd.).

[0037] The titanium black may be produced by, for example, a method in which a mixture of titanium dioxide and metal titanium is heated and reduced in a reducing atmosphere (see, for example, JP-A No. 49-5432), a method in which titanium tetrachloride is hydrolyzed at high temperature to obtain ultrafine titanium dioxide and the obtained titanium dioxide is reduced in a reducing atmosphere containing hydrogen (see, for example, JP-A No. 57-205322), a method in which titanium dioxide or titanium hydroxide is reduced at high temperature in the presence of ammonia (see, for example, JP-A No. 60-65069, JP-A No. 61-201610), and a method in which a vanadium compound is adhered to titanium dioxide or titanium hydroxide and the resultant is then reduced at high temperature in the presence of ammonia (see, for example, JP-A No. 61-201610), but the invention is not limited thereto.

[0038] The particle diameter of titanium black particles is not particularly limited, but it is preferably from 3 nm to 2,000 nm, more preferably from 10 nm to 500 nm, and most preferably 10 nm to 100 nm, from the viewpoints of dispersibility and colorability. Further, the average primary particle diameter of titanium black particles is not particularly limited, but is preferably from 3 nm to 2000 nm, more preferably from 10 nm to 500 nm, and most preferably from 10 nm to 100 nm, from the viewpoints of dispersibility and colorability.

A specific area of the titanium black is not specifically limited. However, in order that a water repellent property has a prescribed performance after the titanium black is surface-treated by a water repellent agent, it is preferred that the titanium black has a surface area measured by the BET method of generally from about 5 m²/g to 150 m²/g, and preferably from about 20 m²/g to 100 m²/g.

[0039] The average particle diameter of the inorganic pigment in the invention is preferably from 5 nm to 0.01 mm, and from the viewpoints of dispersibility, light-shielding property, and sedimentation property over time, the average particle diameter is more preferably from 10 nm to 1 μm.

The black polymerizable composition of the invention may include only a single species of the black material, or a combination of two or more kinds thereof. Further, as described below, an organic pigment, a dye, or the like may be used in combination therewith, if necessary, for the purpose of adjusting the light-shielding property or the like.

The content of the black material in the black polymerizable composition is preferably from 5% by mass to 70% by mass, and more preferably from 10% by mass to 50% by mass, with respect to the total solid content.

[0040] *Pigment Dispersant*

When the black polymerizable composition is formulated using a pigment as a (A) black material, it is preferable that the pigment be dispersed in advance with a known pigment dispersant to prepare a pigment dispersion, and the pigment dispersion is blended, from the viewpoints of the uniformity of the obtained composition.

As the pigment dispersant (hereinafter also simply referred to as a “dispersant”), for example, a known pigment dispersant or a surfactant may be appropriately selected and used.

[0041] Specifically, various types of compounds may be used as the dispersant. Examples thereof include: cationic surfactants such as organosiloxane polymer KP341 (trade name, manufactured by Shin-Etsu Chemical Co., Ltd.), (meth)acrylic acid (co)polymer POLYFLOW No. 75, No. 90, No. 95 (trade names, manufactured by Kyoeisha Chemical Co., Ltd.), or W001 (trade name, available from Yusho Co., Ltd.); nonionic surfactants such as polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene nonyl phenyl ether, polyethylene glycol dilaurate, polyethylene glycol distearate, or sorbitan fatty acid ester; anionic surfactants such as W004, W005, or W017 (trade names, manufactured by Yusho Co., Ltd.); polymeric dispersants such as EFKA-46, EFKA-47, EFKA-47EA, EFKA POLYMER 100, EFKA POLYMER 400, EFKA POLYMER 401, EFKA POLYMER 450 (trade names, manufactured by BASF Corporation), DISPERSE AID 6, DISPERSE AID 8, DISPERSE AID 15, or DISPERSE AID 9100 (trade names, manufactured by San Nopco Limited); various SOLSPERSE dispersants such as SOLSPERSE 3000, 5000, 9000, 12000, 13240, 13940, 17000, 24000, 26000, 28000, 32000 or 36000 (trade names, manufactured by The Lubrizol Corporation); ADEKA PLURONIC L31, F38, L42, L44, L61, L64, F68, L72, P95, F77, P84, F87, P94, L101, P103, F108, L121, P-123 (trade names, manufactured by ADEKA Corporation); IONET S-20 (trade name, manufactured by Sanyo Chemical Industries, Ltd.); and DISPERBYK 101, 103, 106, 108, 109, 111, 112, 116, 130, 140, 142, 162, 163, 164, 166, 167, 170, 171, 174, 176, 180, 182, 2000, 2001, 2050, 2150 (trade names, manufactured by BYK-Chemie).

In addition, other examples of the dispersant include oligomers and polymers having a polar group at an end or a side chain of the molecules, such as acrylic copolymers.

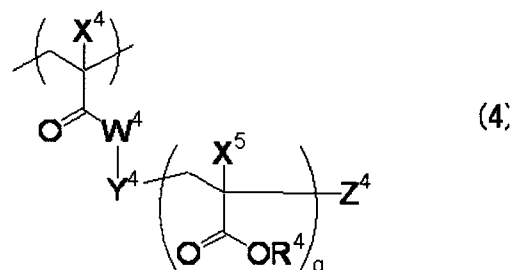
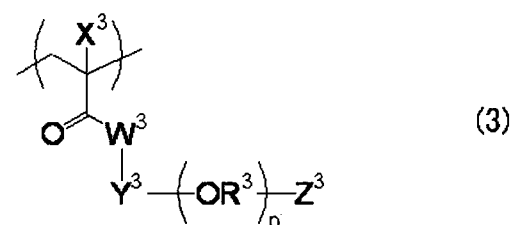
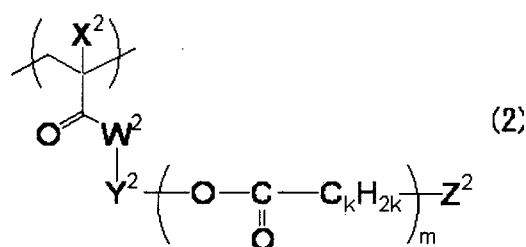
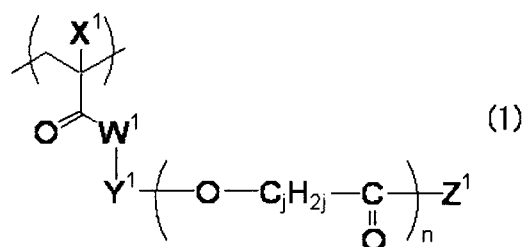
Furthermore, amphoteric dispersants such as HINOACT T-8000E (trade name, manufactured by Kawaken Fine Chemicals Co., Ltd.) may be suitably used.

From the viewpoints of dispersibility, developability, and sedimentation property, a resin shown below, as described in JP-A No. 2010-106268, is preferable, particularly, from the viewpoints of dispersibility, a polymeric dispersant having a polyester chain at a side chain is preferable. From the viewpoints of dispersibility and resolution of a pattern formed by photolithography, a resin having an acid group and a polyester chain is preferable. As the acid group preferable in the pigment dispersant, an acid group having a pKa of 6 or less is preferable from the viewpoints of adsorptivity, and carboxylic acid, sulfonic acid, or phosphoric acid is particularly preferable. From the viewpoints of solubility in a dispersion solution, dispersibility, and developability, a resin having a polycaprolactone side chain as a polyester chain and having a carboxylic acid group is most preferable.

[0042] Hereinbelow, the dispersant as described in JP-A No. 2010-106268, which is preferably used in the invention, will be explained.

A preferable dispersant is a graft copolymer which has the number of the atoms excluding hydrogen atoms in the molecule ranging from 40 to 10,000, has a graft chain selected from a polyester structure, a polyether structure, and a polyacrylate structure, and includes any one of the structural units represented by Formulae (1) to (4) shown below, and the graft copolymer which includes a structural unit represented by any one of the following Formulae (1A), (2A), (3A), (3B), and (4) is more preferable.

[0043]



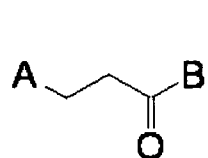
[0044] In Formulae (1) to (4), each of W^1 , W^2 , W^3 and W^4 independently represents an oxygen atom or NH, and particularly preferably an oxygen atom.

In Formulae (1) to (4), each of X^1 , X^2 , X^3 , X^4 and X^5 independently represents a hydrogen atom or a monovalent organic group. From the viewpoint of limitation of

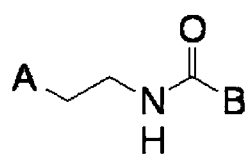
synthesis, each of X^1 , X^2 , X^3 , X^4 and X^5 independently represents preferably a hydrogen atom or an alkyl group having 1 to 12 carbon atoms, more preferably a hydrogen atom or a methyl group, and particularly preferably a methyl group.

In Formulae (1) to (4), each of Y^1 , Y^2 , Y^3 and Y^4 independently represents a divalent linking group, and their structures are not particularly limited. Specific examples of the divalent linking groups represented by Y^1 , Y^2 , Y^3 and Y^4 include the linking groups represented by the following structures (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 (1) to (4), 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 (1) to (4). Among the structures shown below, the structures of (Y-2) and (Y-13) are more preferable in terms of the ease of synthesis.

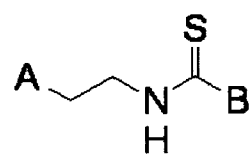
[0045]



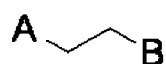
(Y-1)



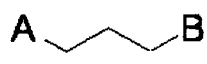
(Y-2)



(Y-3)



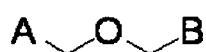
(Y-4)



(Y-5)



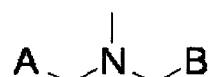
(Y-6)



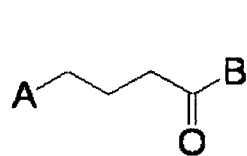
(Y-7)



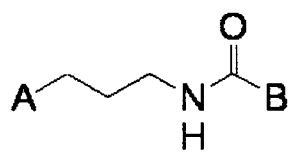
(Y-8)



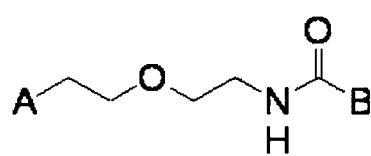
(Y-9)



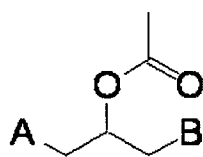
(Y-10)



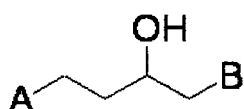
(Y-11)



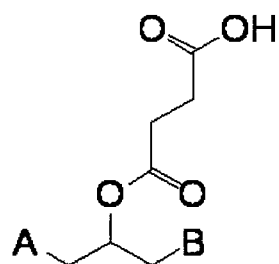
(Y-12)



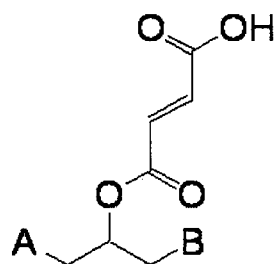
(Y-13)



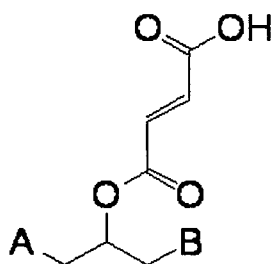
(Y-14)



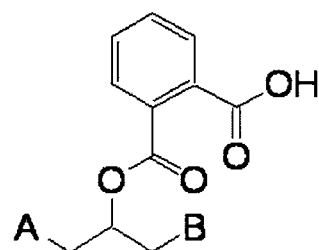
(Y-15)



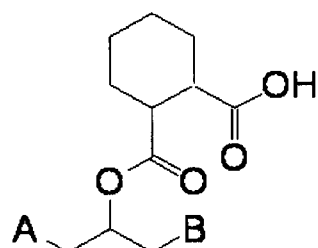
(Y-16)



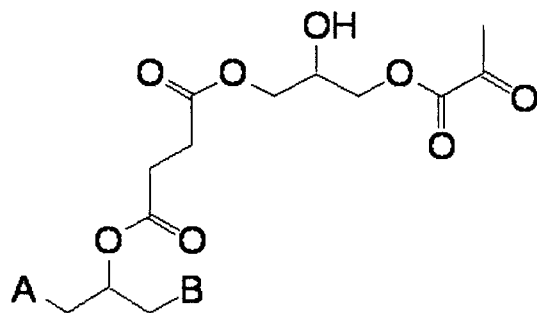
(Y-17)



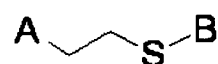
(Y-18)



(Y-19)



(Y-20)



(Y-21)

[0046] In Formulae (1) to (4), Z^1 , Z^2 , Z^3 , and Z^4 each independently represent a monovalent organic group, and their structures are not particularly limited. Specific examples thereof include an alkyl group, a hydroxyl group, an alkoxy group, an aryloxy group or a heteroaryloxy group, an alkylthioether group, an arylthioether group or a heteroarylthioether group, and an amino group. Among these, as the monovalent organic groups represented by Z^1 , Z^2 , Z^3 , and Z^4 , those having a steric repellency property are preferable particularly from the viewpoint of improvement of dispersibility. It is preferable that 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, and particularly preferably an alkoxy group having a branched alkyl group having 5 to 24 carbon atoms or an alkoxy group having a cyclic alkyl group having 5 to 24 carbon atoms. The organic group represented by Z^4 is preferably an alkyl group having 5 to 24 carbon atoms, and particularly preferably a branched alkyl group having 5 to 24 carbon atoms or a cyclic alkyl group having 5 to 24 carbon atoms.

In Formulae (1) to (4), n, m, p, and q are each an integer from 1 to 500.

In Formulae (1) and (2), j and k each independently represent an integer from 2 to 8, and j and k in Formulae (1) and (2) are preferably an integer from 4 to 6, and most preferably 5, from the viewpoints of dispersion stability and developability.

[0047] R^3 in Formula (3) represents a branched or straight-chained alkylene group. R^3 in Formula (3) is preferably an alkylene group having 1 to 10 carbon atoms, and more preferably an alkylene group having 2 or 3 carbon atoms.

R^4 in Formula (4) represents a hydrogen atom or a monovalent organic group, and the structure of the monovalent organic group is not particularly limited. Preferable examples of R^4 in Formula (4) include a hydrogen atom, an alkyl group, an aryl group, and a heteroaryl group, and more preferably, a hydrogen atom and an alkyl group. When R^4 in Formula (4) is an alkyl group, the alkyl group is preferably a straight-chained 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-chained alkyl group having 1 to 20 carbon atoms, and particularly preferably a straight-chained alkyl group having 1 to 6 carbon atoms. Further, regarding R^4 in Formula (4), two or more kinds of R^4 's having different structures may be mixed and used in a graft copolymer.

[0048] In the graft copolymer, the content (i.e., total content) of the structure units represented by Formulae (1) to (4) is preferably in the range of from 10% to 90%, and more preferably from 30% to 70%, with respect to the total mass of the graft copolymer. When the structure units represented by Formulae (1) to (4) are included within these ranges, the dispersibility of the pigment is high and the developability when a light-shielding film is

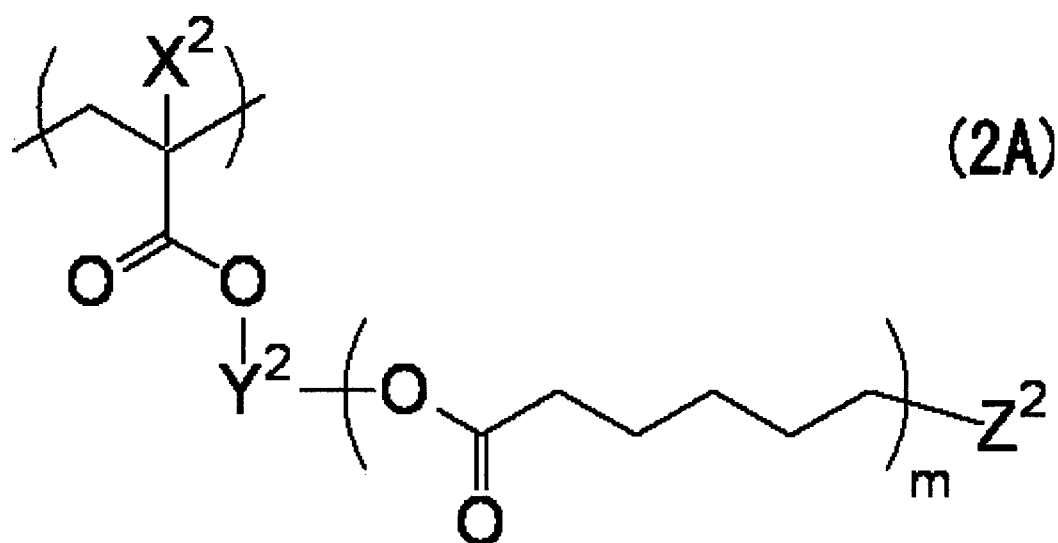
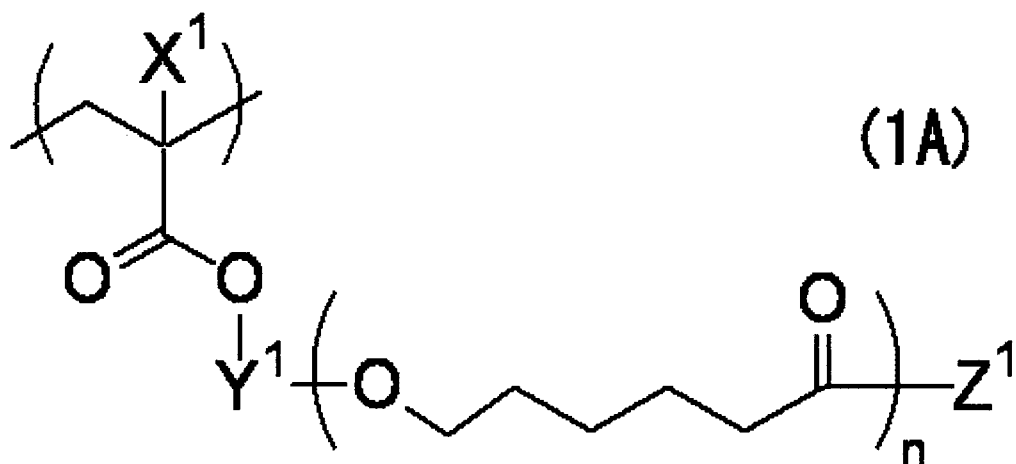
formed is good.

[0049] The graft copolymer may include two or more kinds of graft copolymers having different structures.

[0050] The structural unit represented by Formula (1) is more preferably a structural unit represented by the following Formula (1A) from the viewpoints of dispersion stability and developability.

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

[0051]



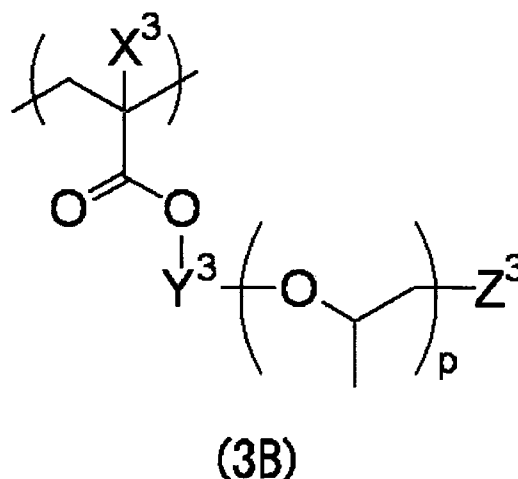
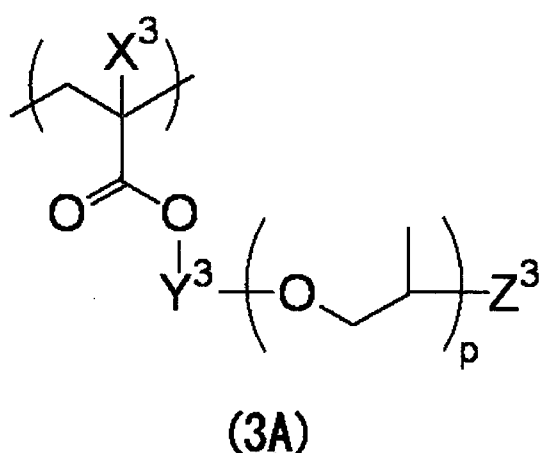
[0052] In Formula (1A), X¹, Y¹, Z¹, and n have the same definitions as X¹, Y¹, Z¹, and n in Formula (1), respectively, and preferable scopes thereof (including examples and the like

thereof) are also the same.

In Formula (2A), X^2 , Y^2 , Z^2 , and m have the same definitions as X^2 , Y^2 , Z^2 , and m in Formula (2), respectively, and preferable scopes thereof (including examples and the like thereof) are also the same.

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

[0053]



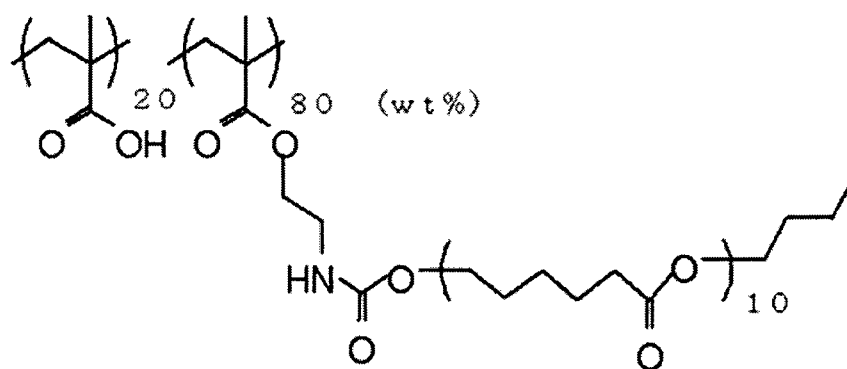
[0054] In Formula (3A) or (3B), X^3 , Y^3 , Z^3 , and p have the same definitions as X^3 , Y^3 , Z^3 , and p in Formula (3), respectively, and preferable ranges thereof (including examples and the like thereof) are also the same.

[0055] It is more preferable that the graft copolymer has the structural unit represented by Formula (1A).

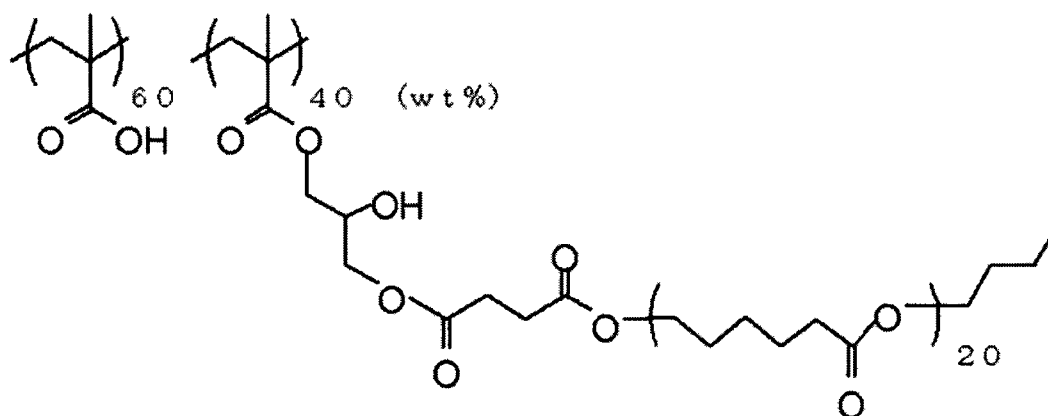
[0056] Specific examples of the graft copolymer include the compounds shown below.

Further, in the exemplary compounds shown below, the numeral values shown together with the respective structural units denote the contents (% by mass: appropriately denoted as (wt%)) of the corresponding structural units.

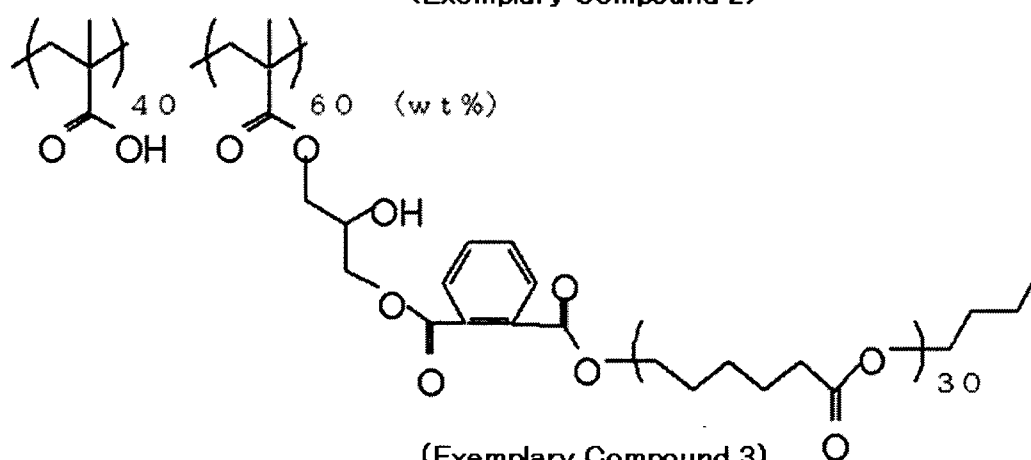
[0057]



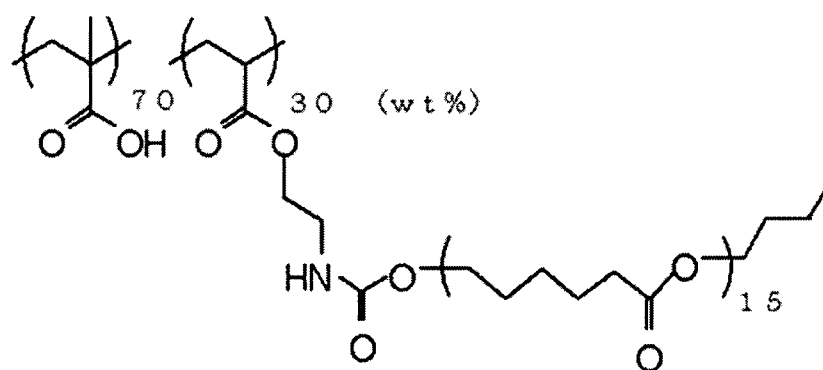
(Exemplary Compound 1)



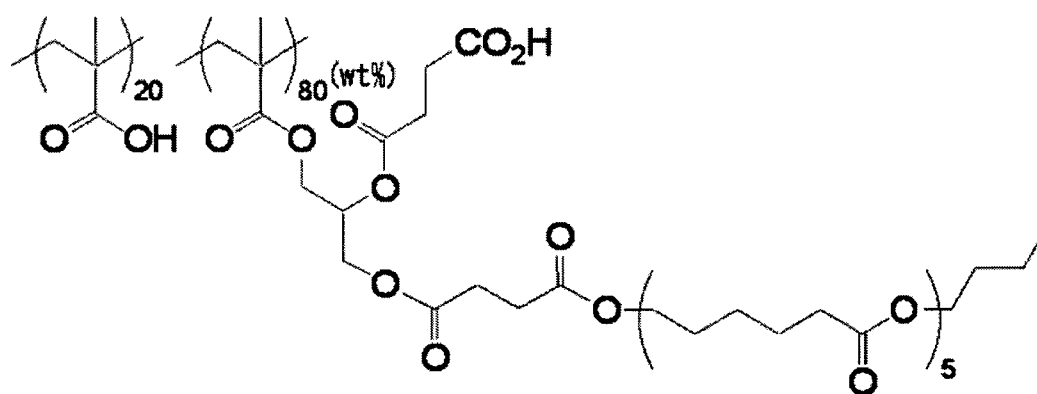
(Exemplary Compound 2)



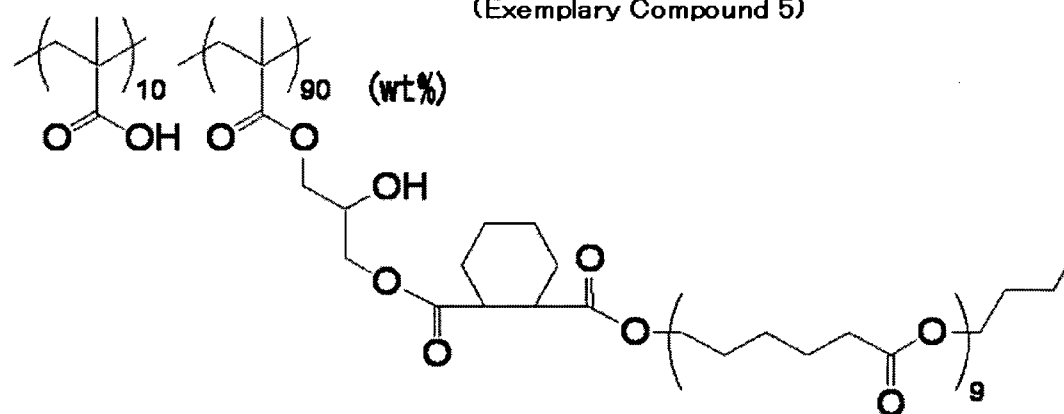
(Exemplary Compound 3)



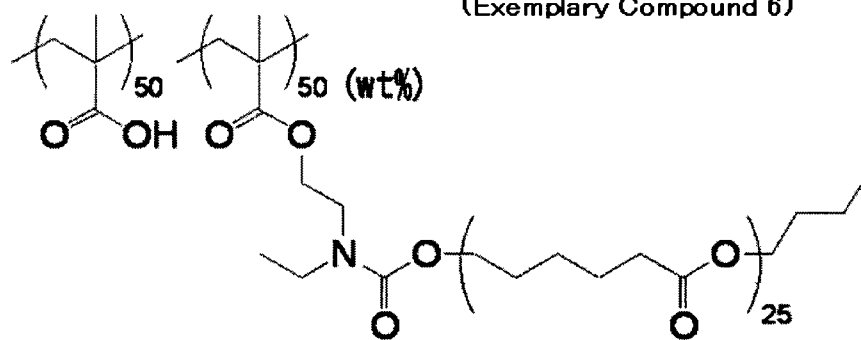
(Exemplary Compound 4)



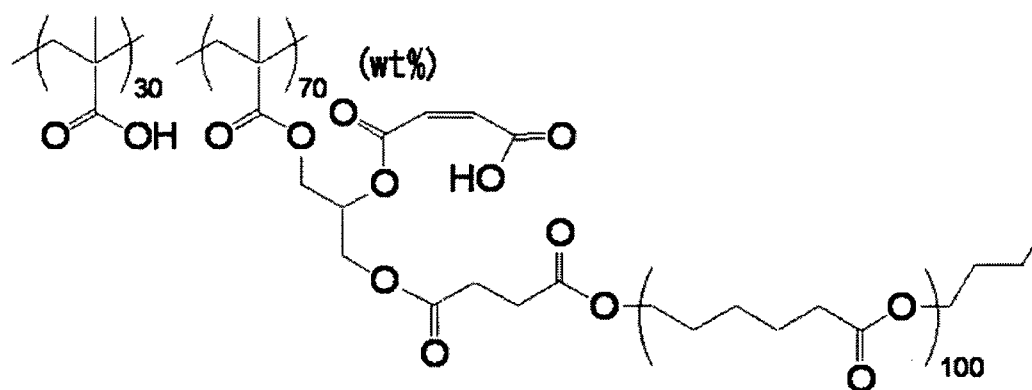
(Exemplary Compound 5)



(Exemplary Compound 6)

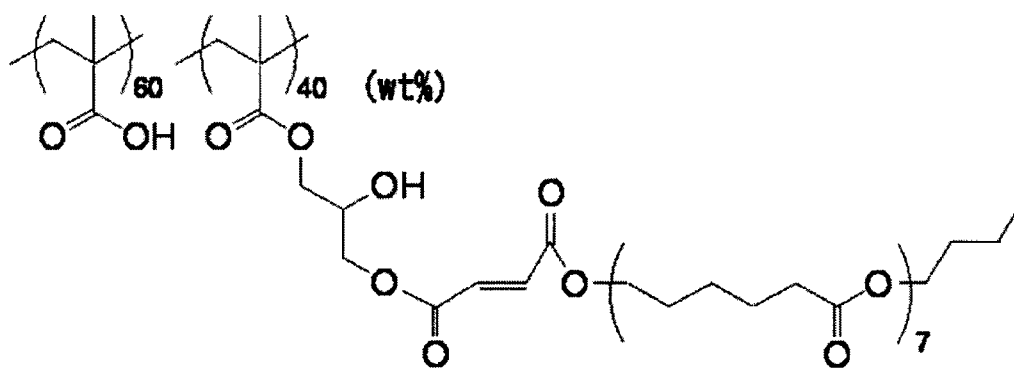


(Exemplary Compound 7)

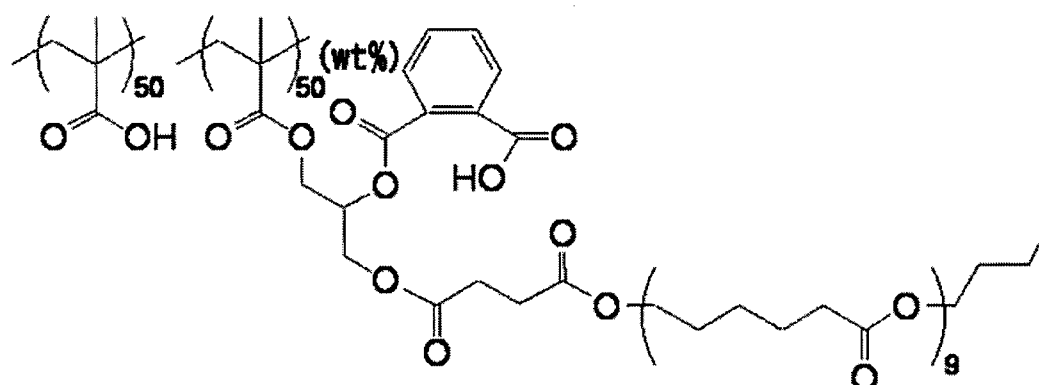


(Exemplary Compound 8)

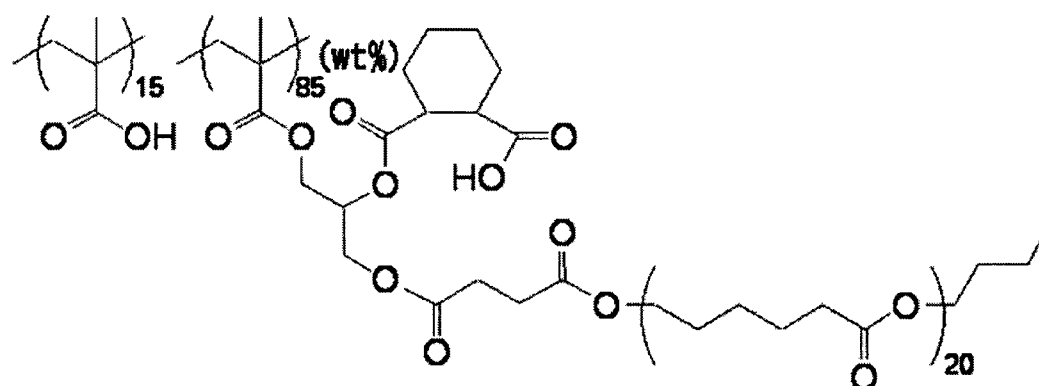
[0059]



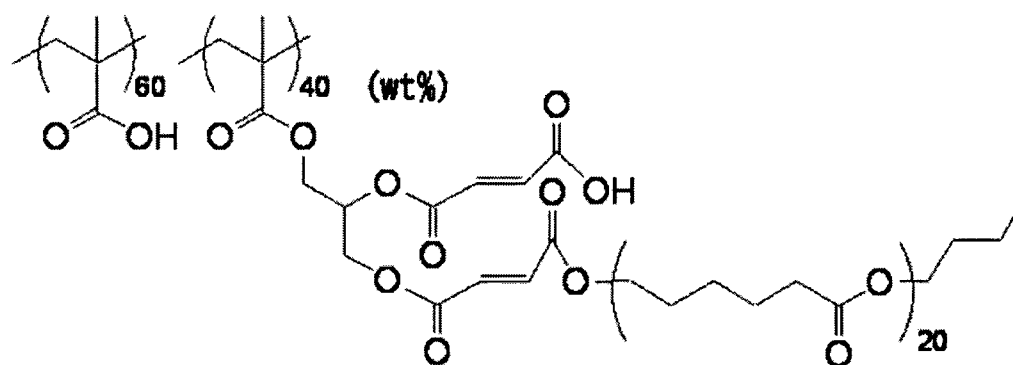
(Exemplary Compound 9)



(Exemplary Compound 10)



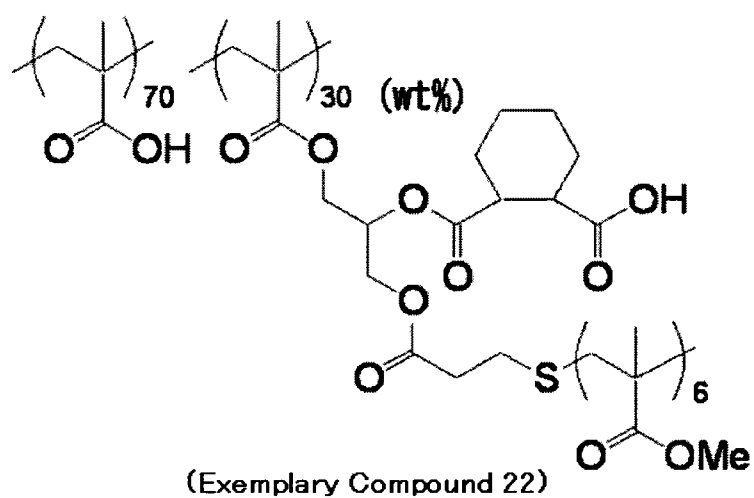
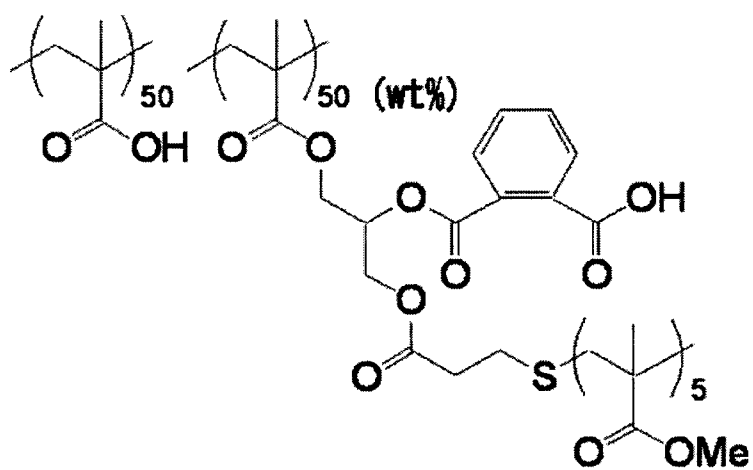
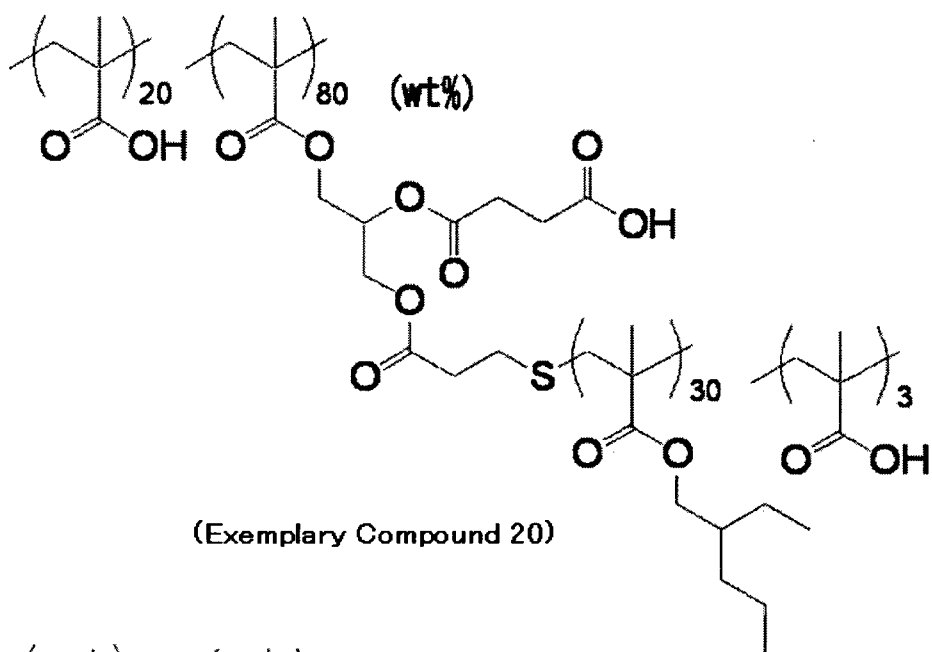
(Exemplary Compound 11)



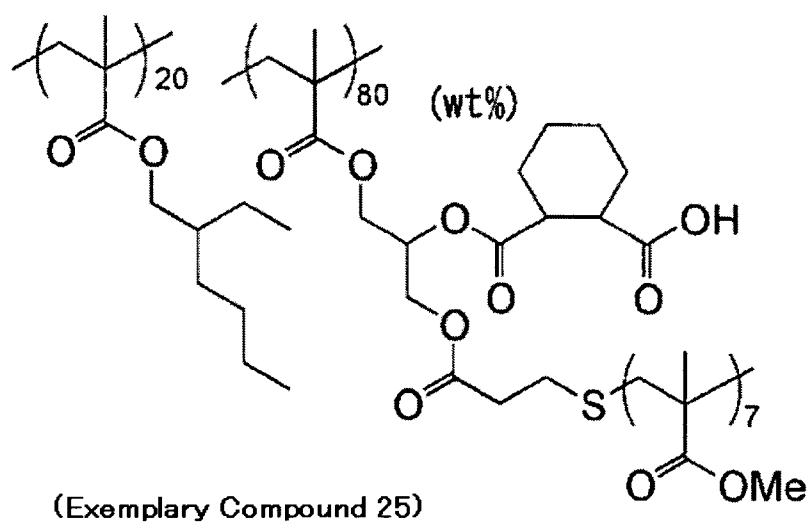
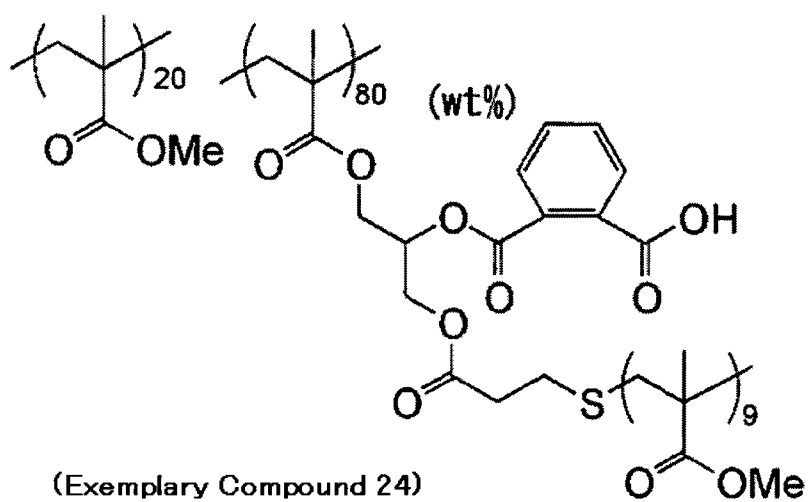
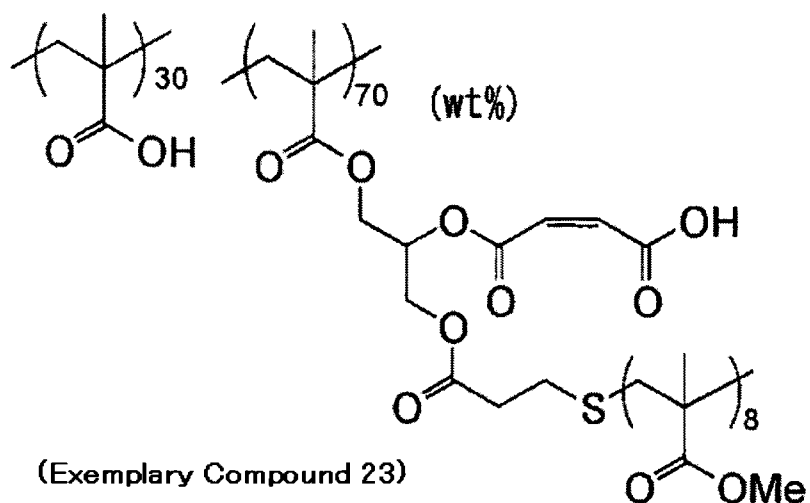
(Exemplary Compound 12)

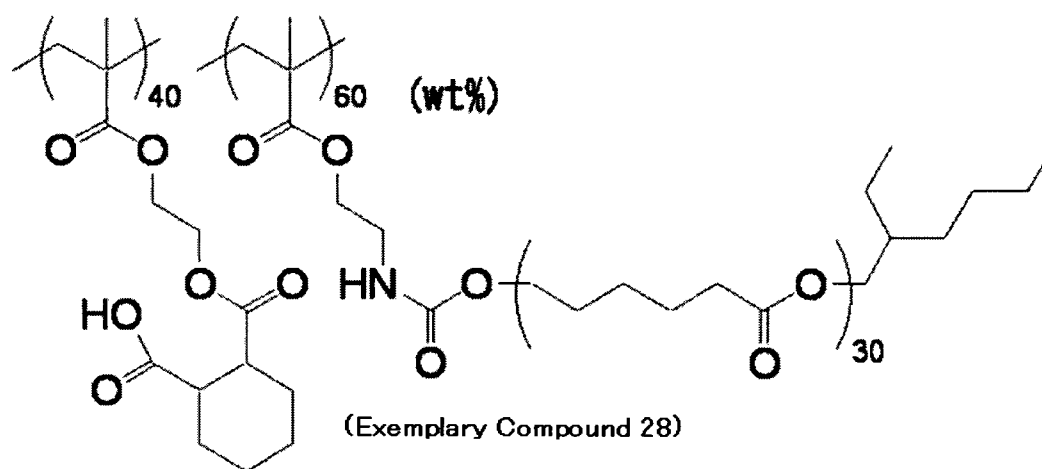
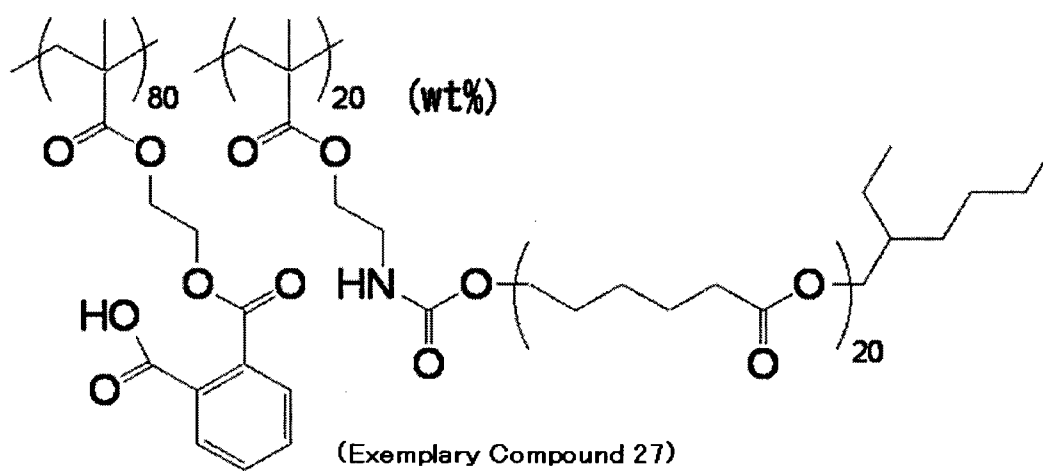
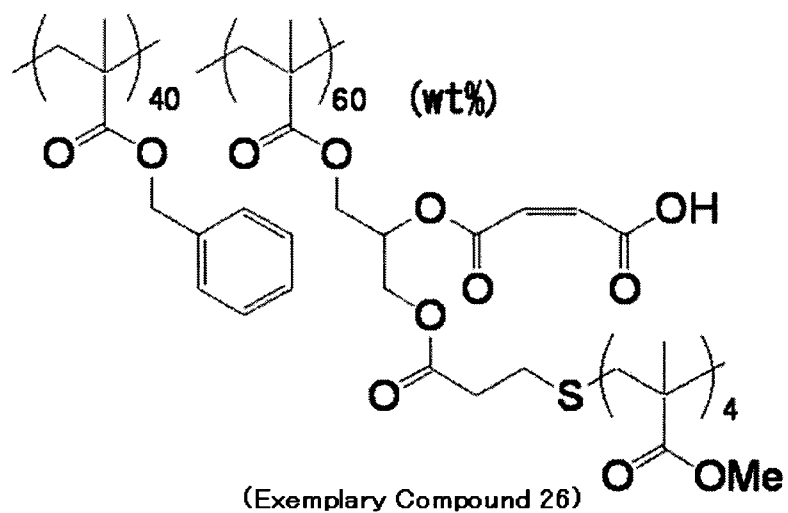


[0061]

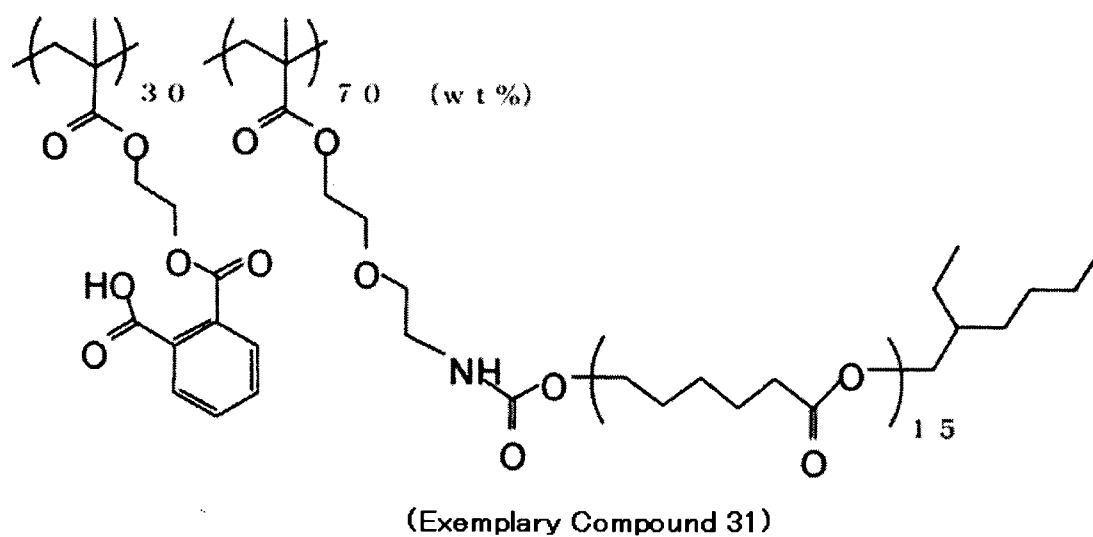
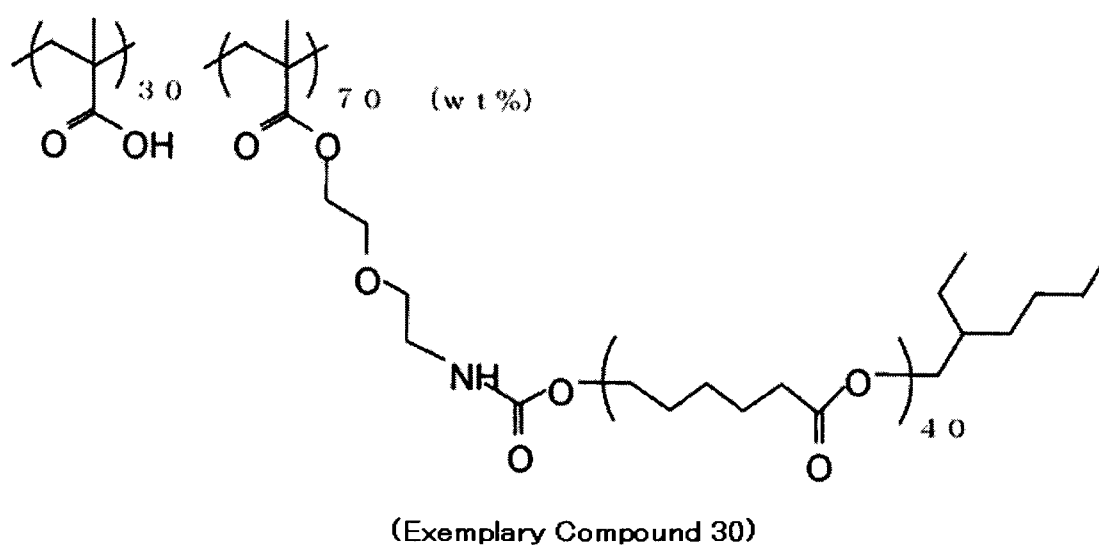
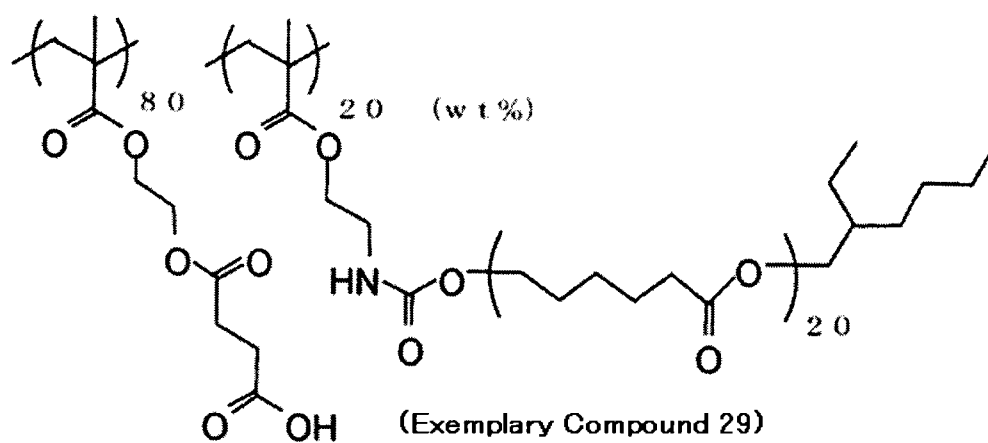


[0062]

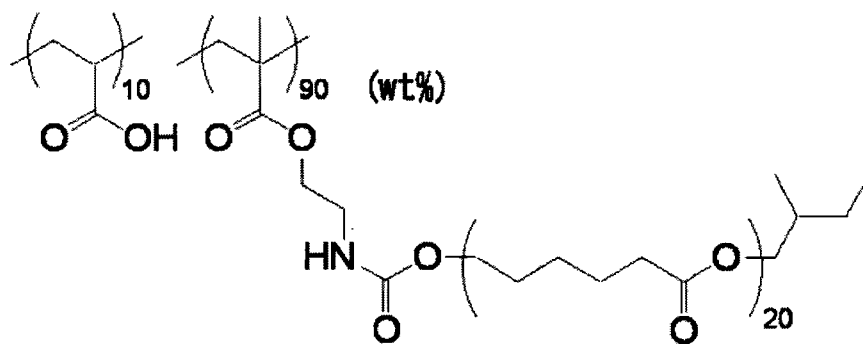
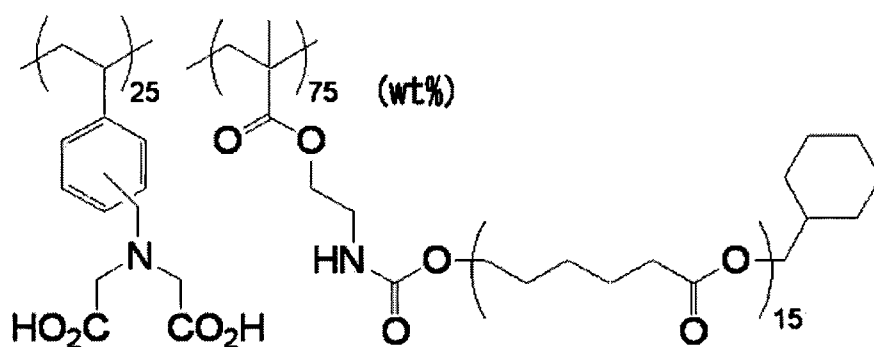
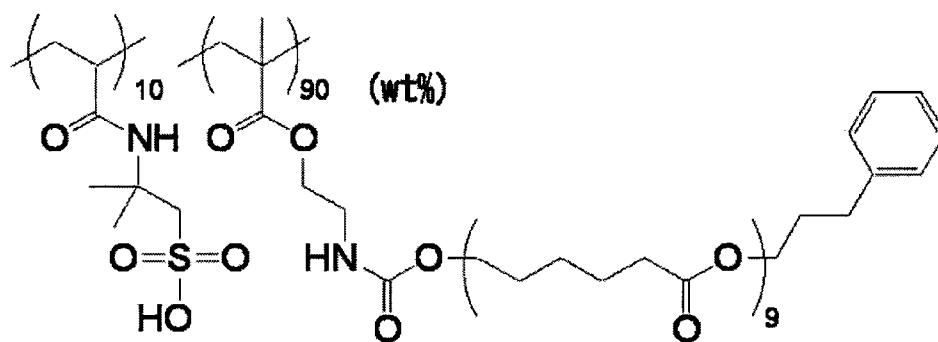
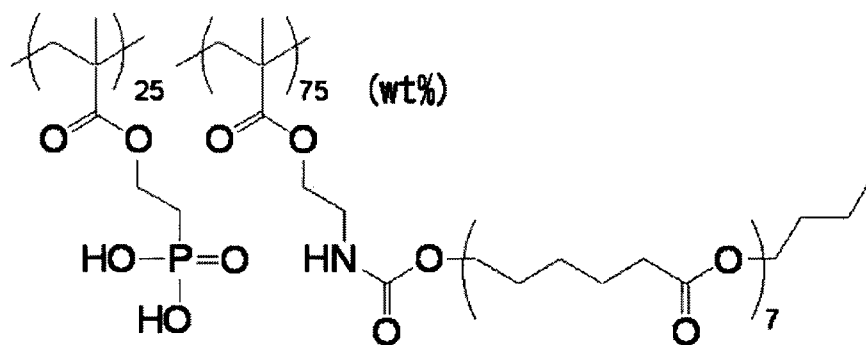




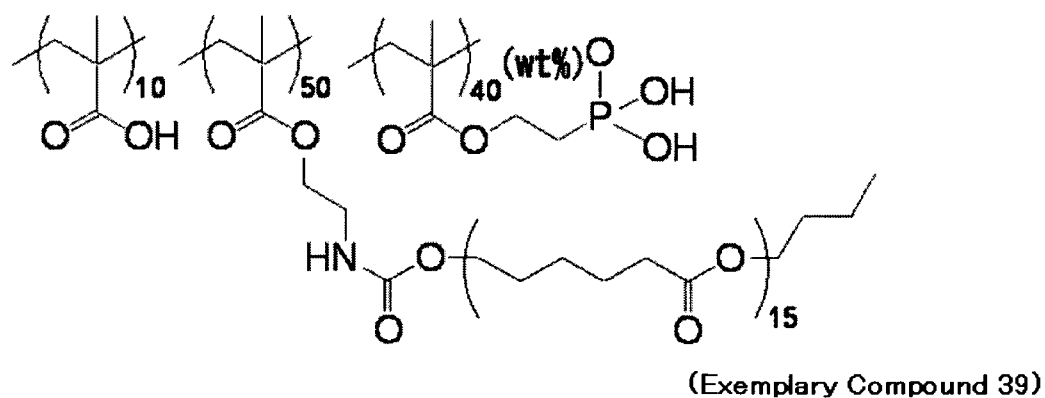
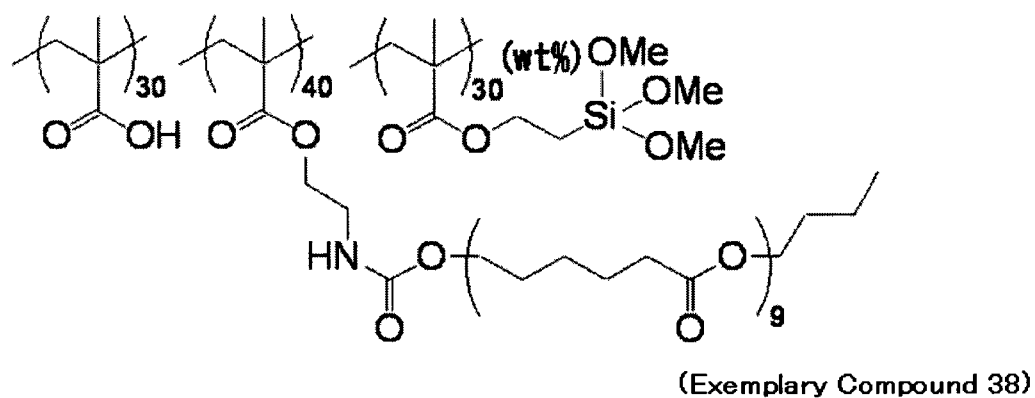
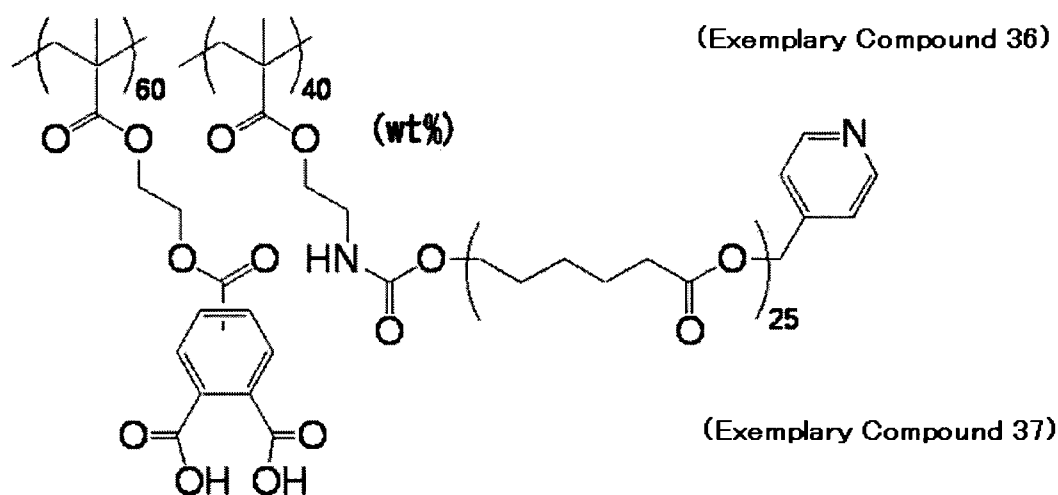
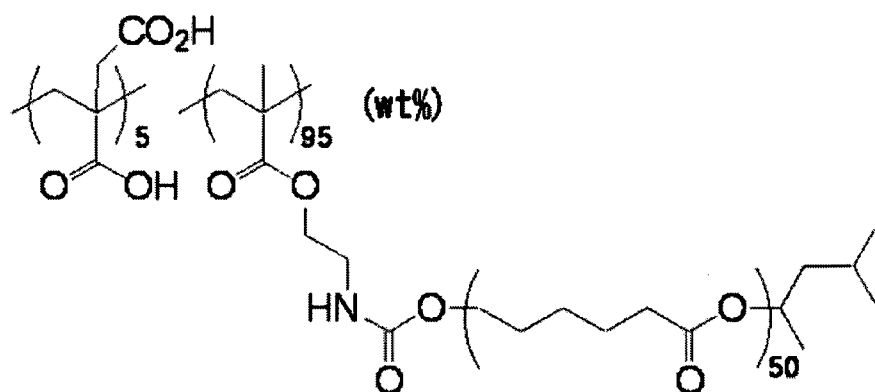
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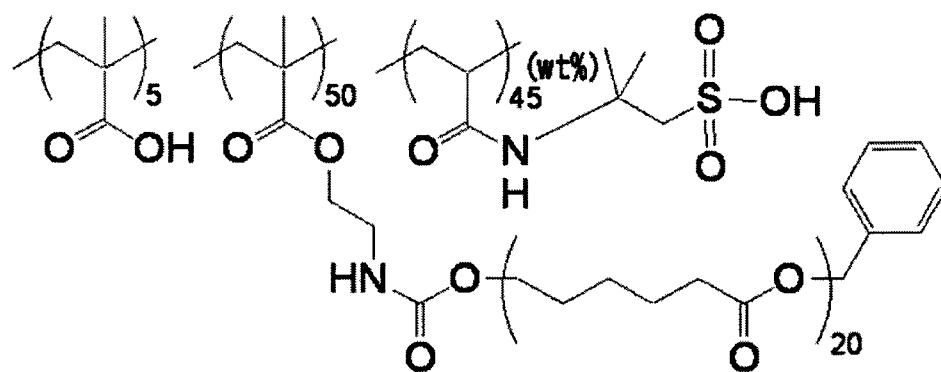


[0065]

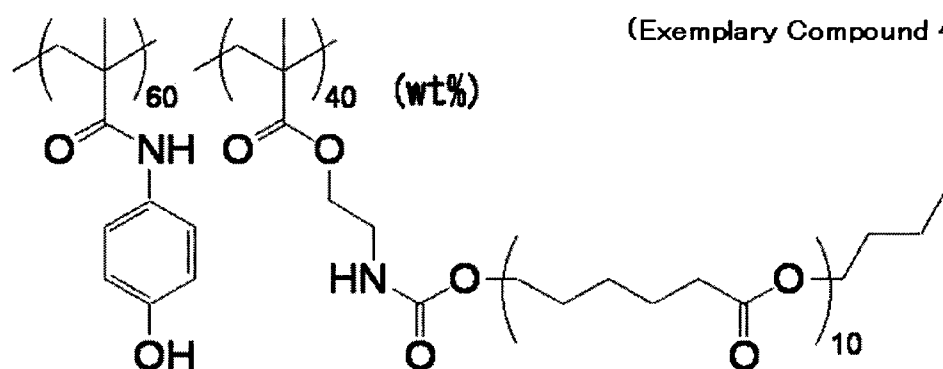


[0066]

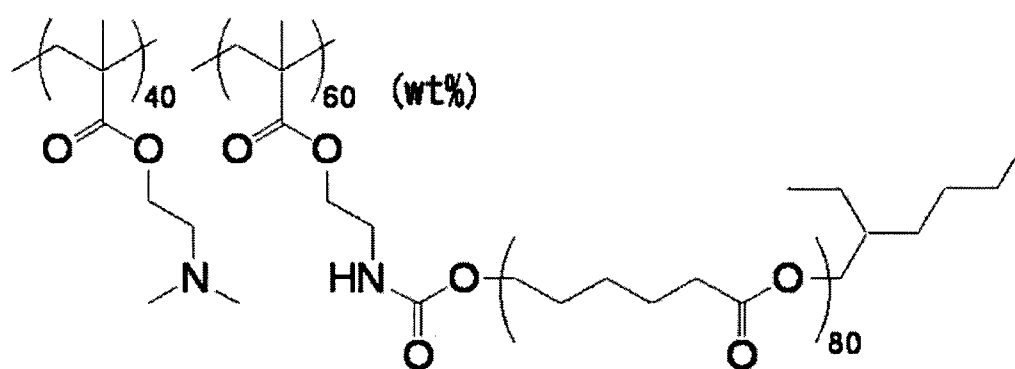




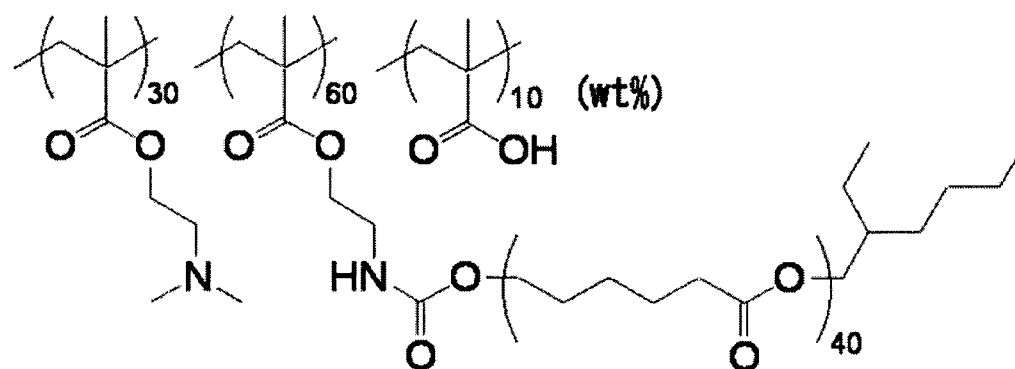
(Exemplary Compound 40)



(Exemplary Compound 41)

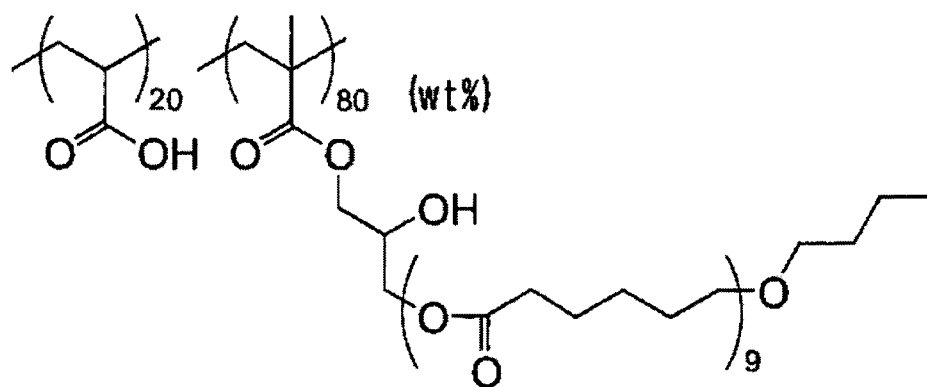


(Exemplary Compound 42)

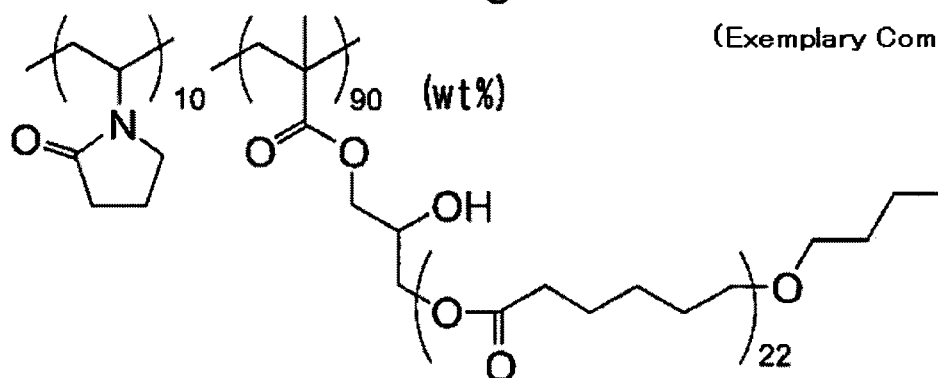


(Exemplary Compound 43)

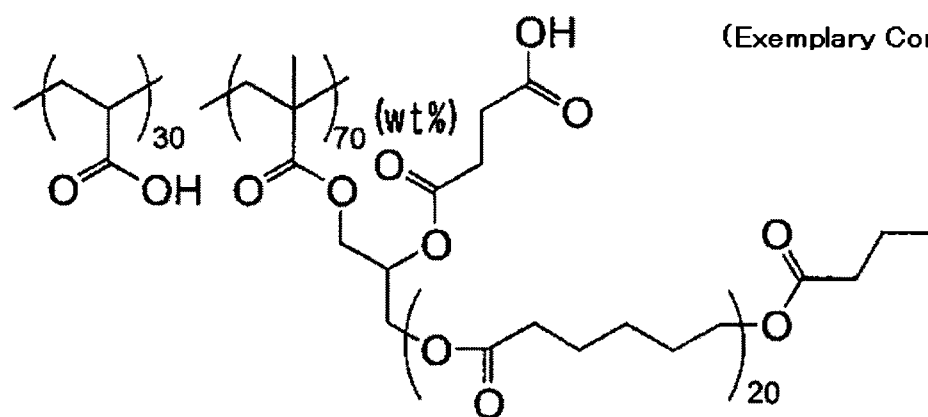
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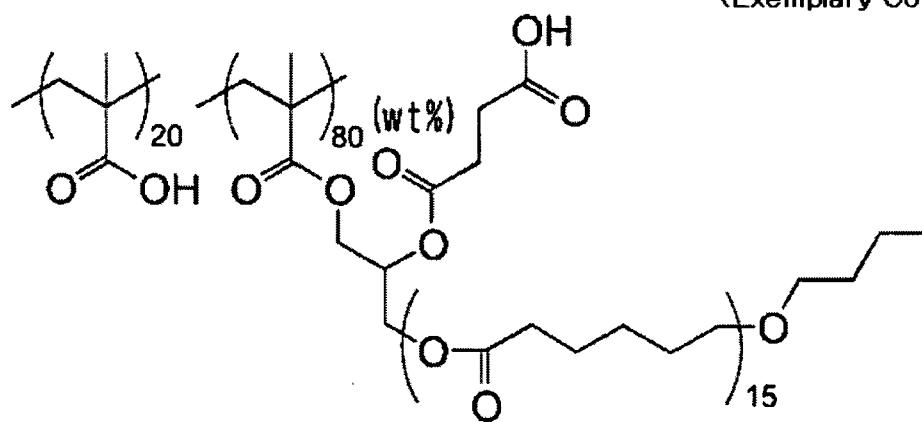
(Exemplary Compound 48)



(Exemplary Compound 49)

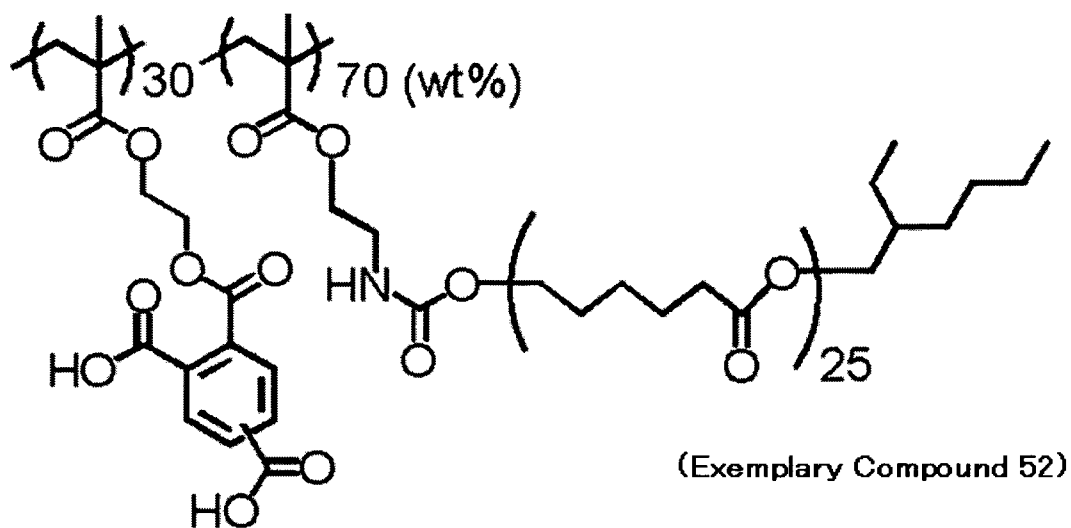


(Exemplary Compound 50)

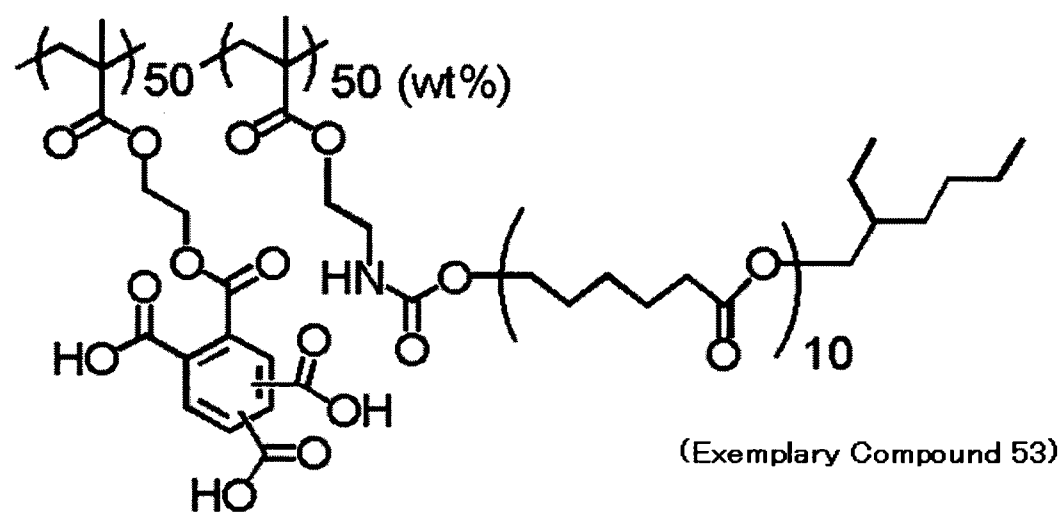


(Exemplary Compound 51)

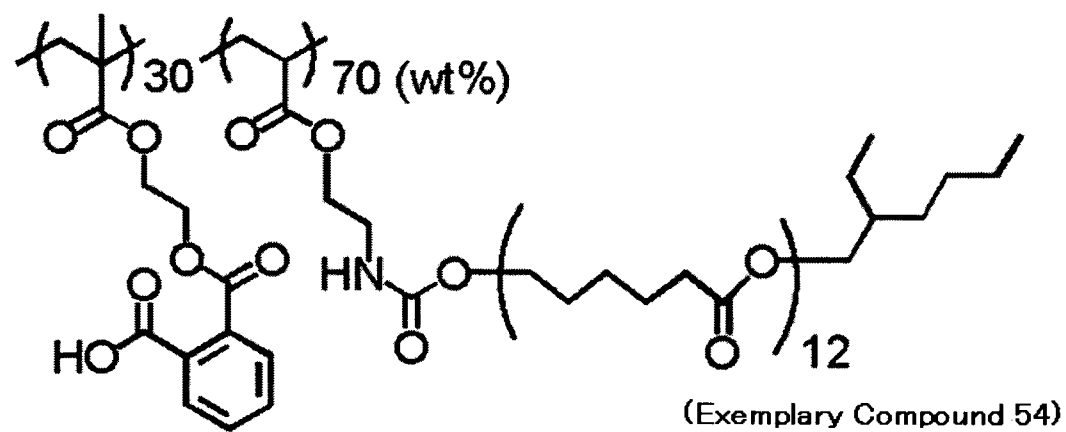
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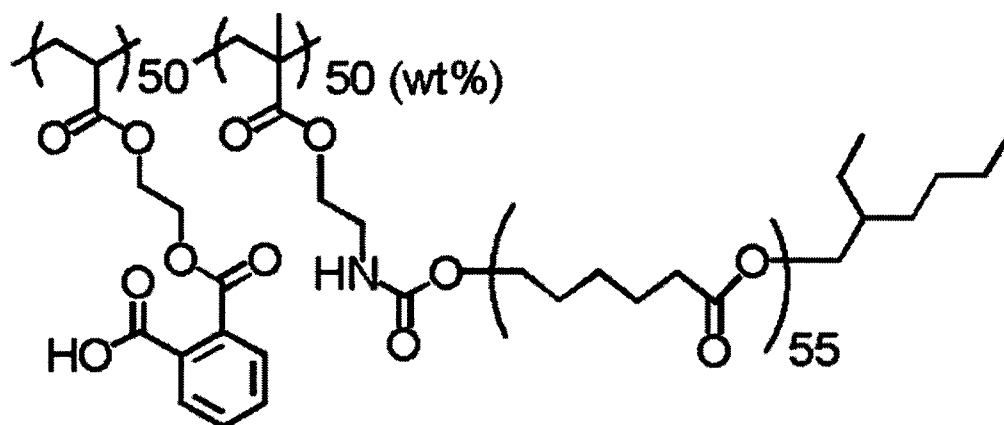
[0071]



[0072]

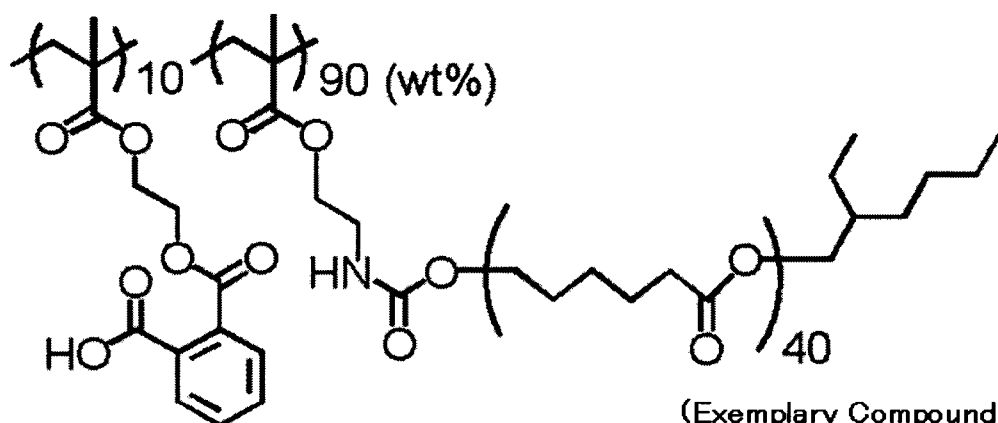


[0073]



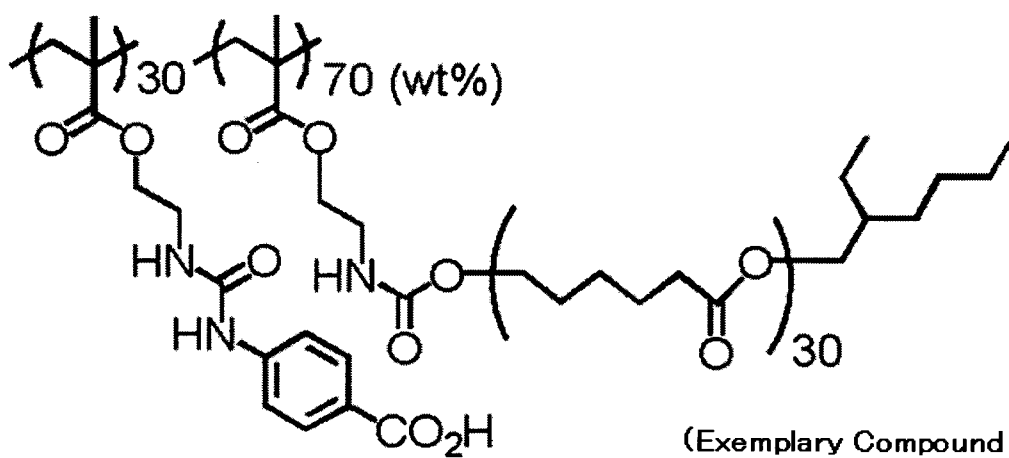
(Exemplary Compound 55)

[0074]



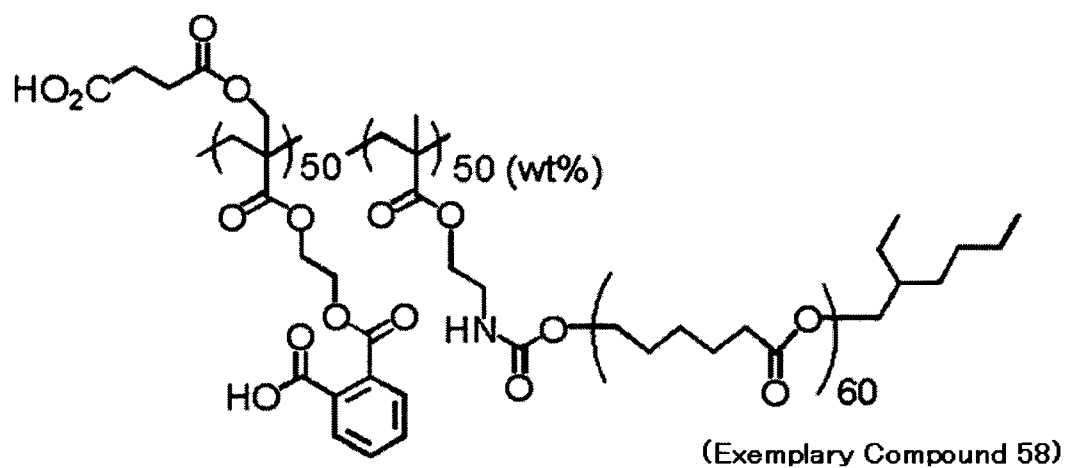
(Exemplary Compound 56)

[0075]

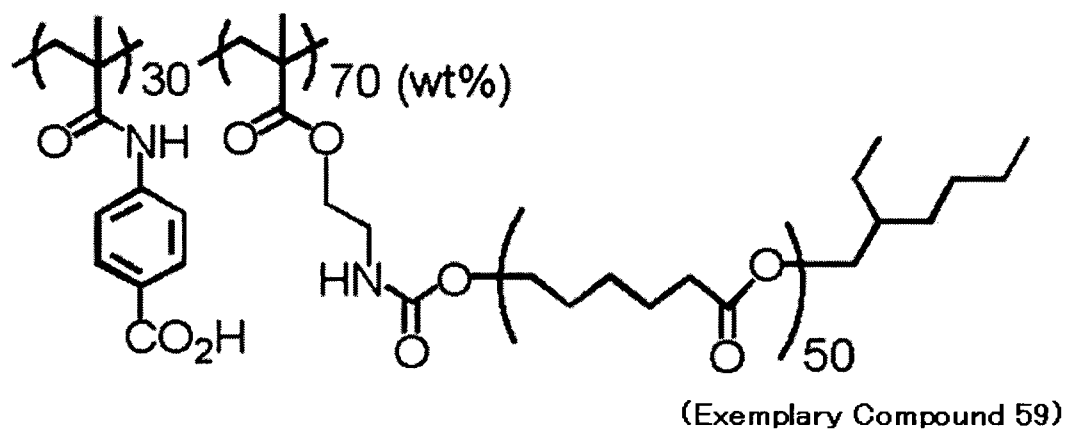


(Exemplary Compound 57)

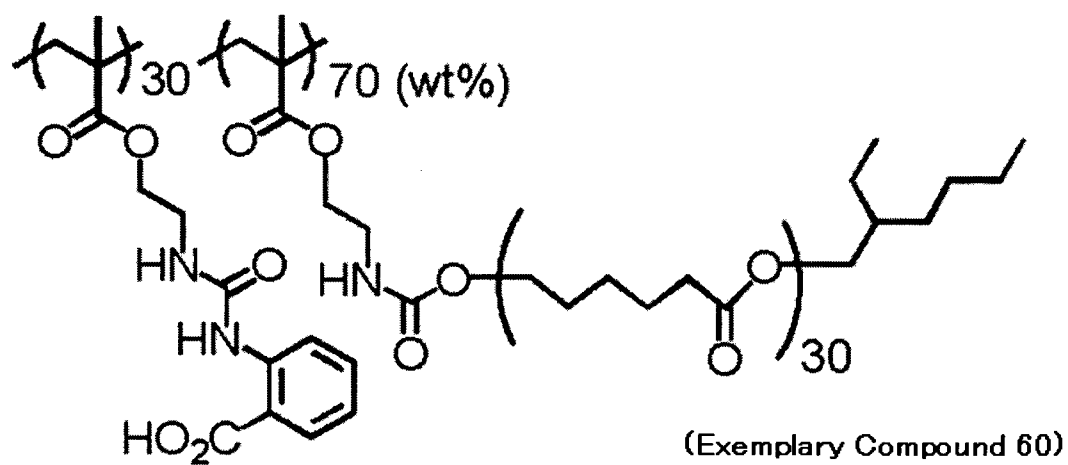
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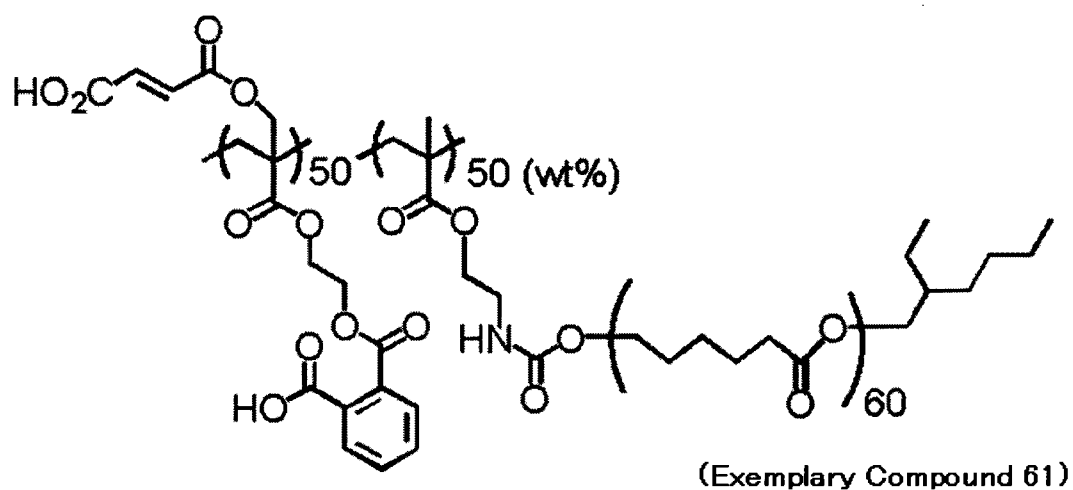
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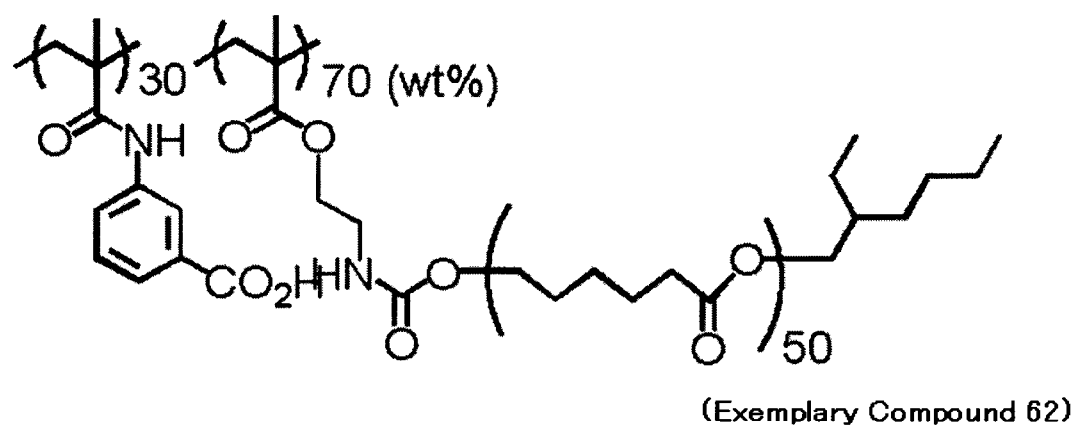
[0078]



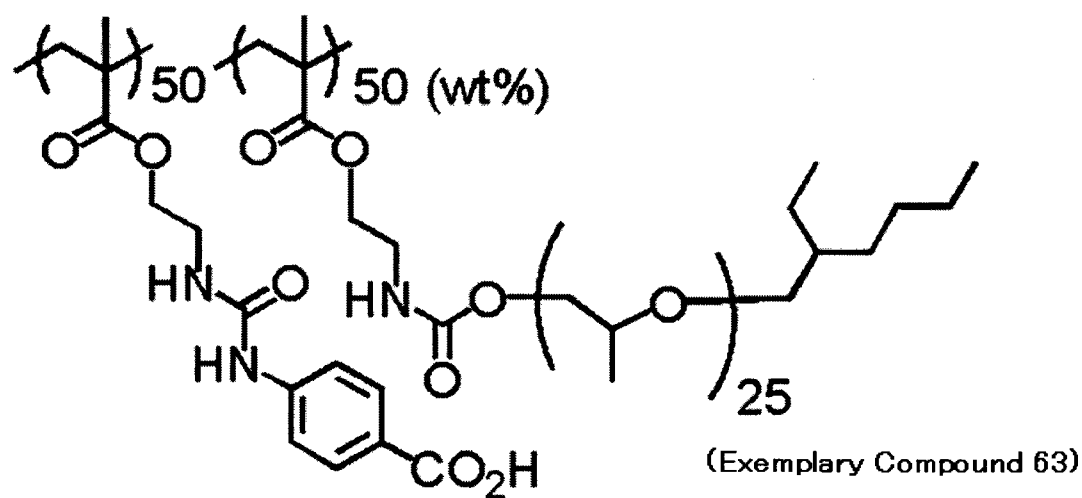
[0079]



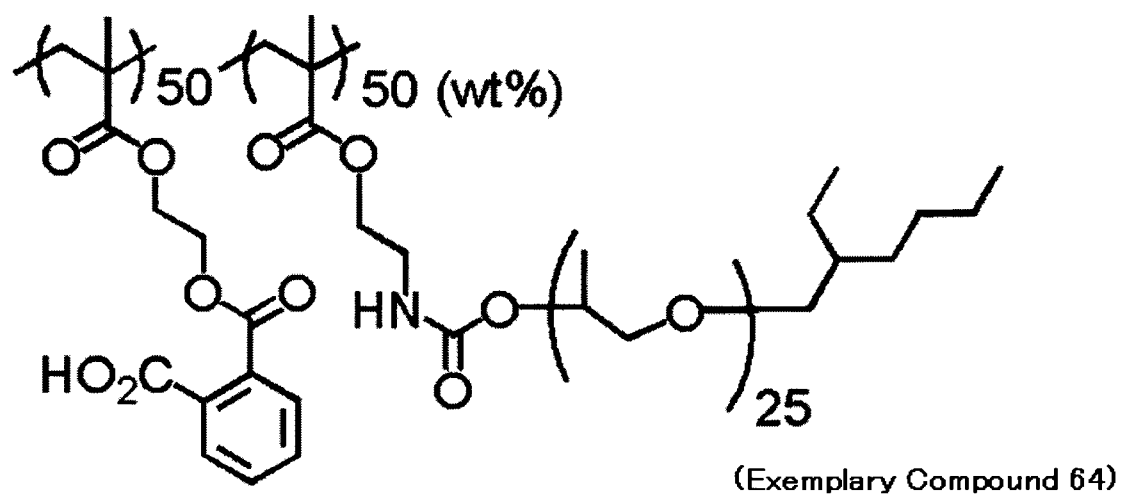
[0080]



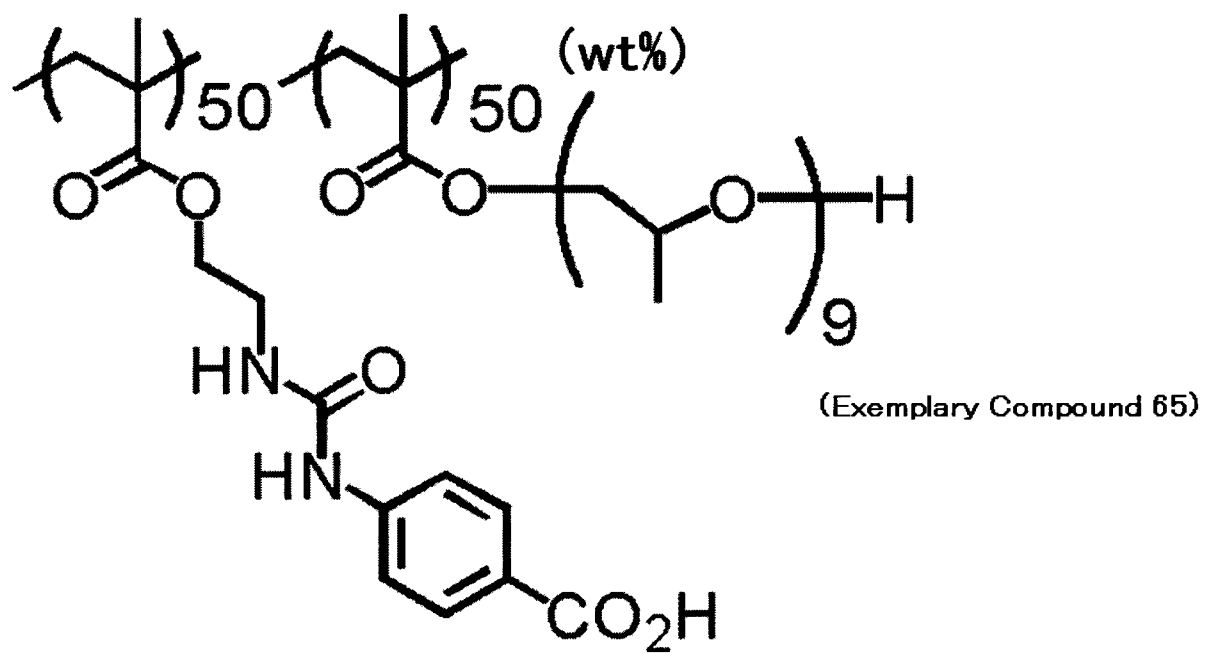
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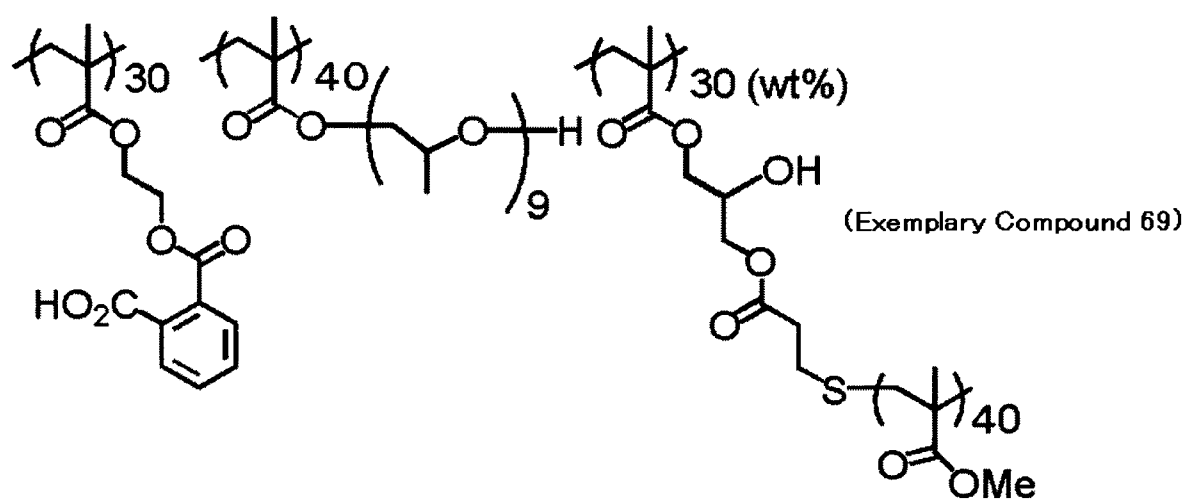


[0082]

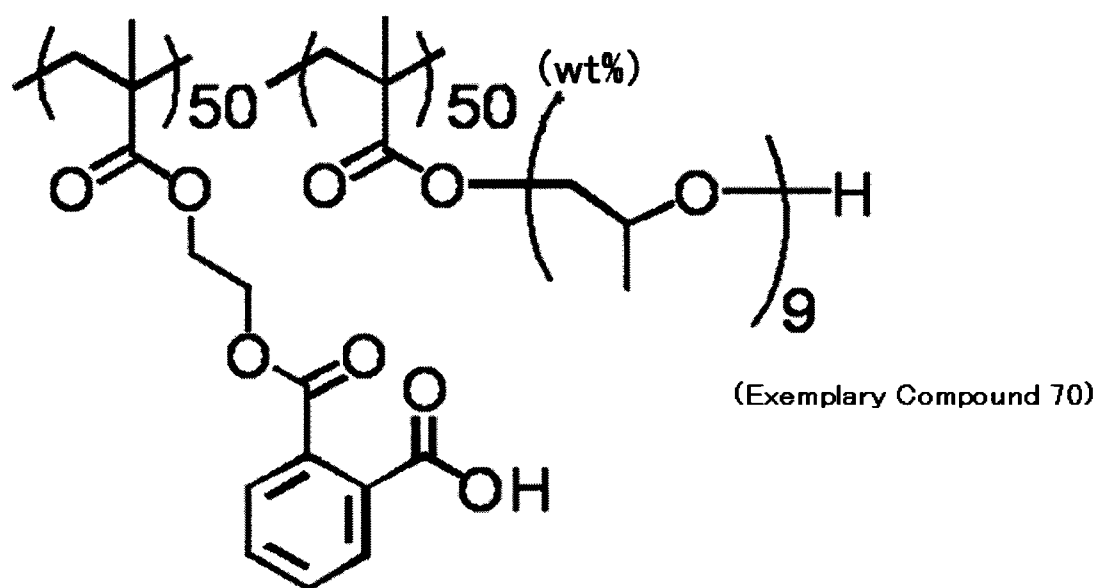


[0083]

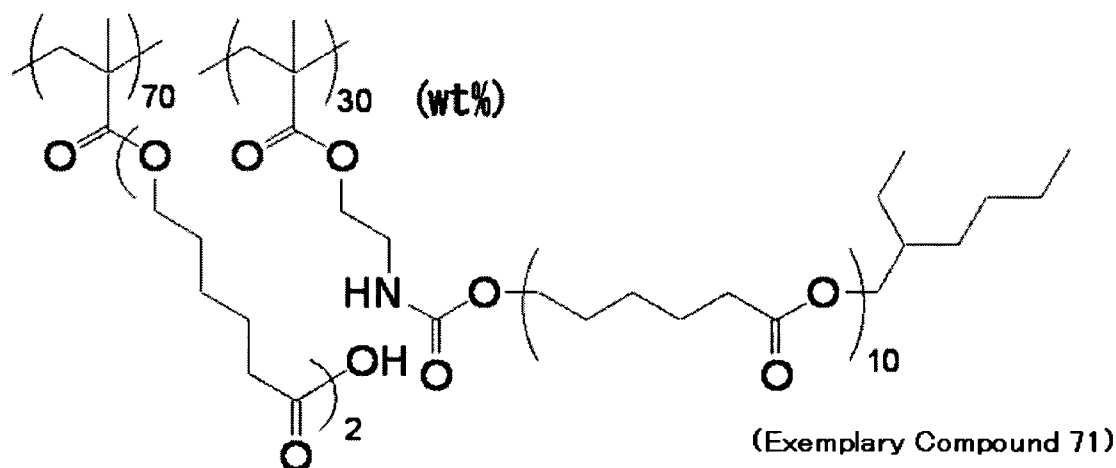




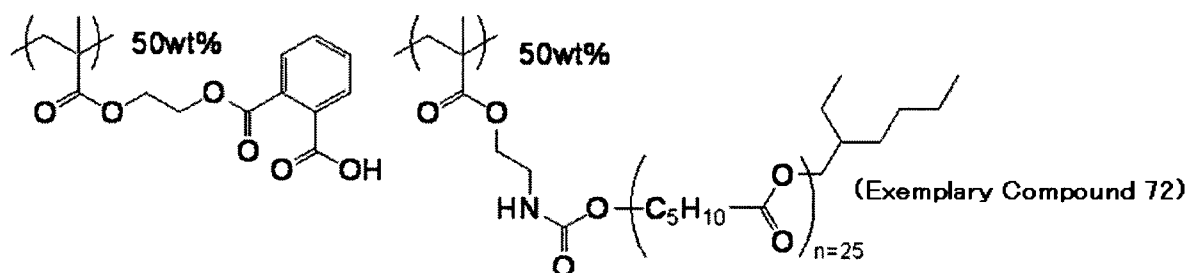
[0088]



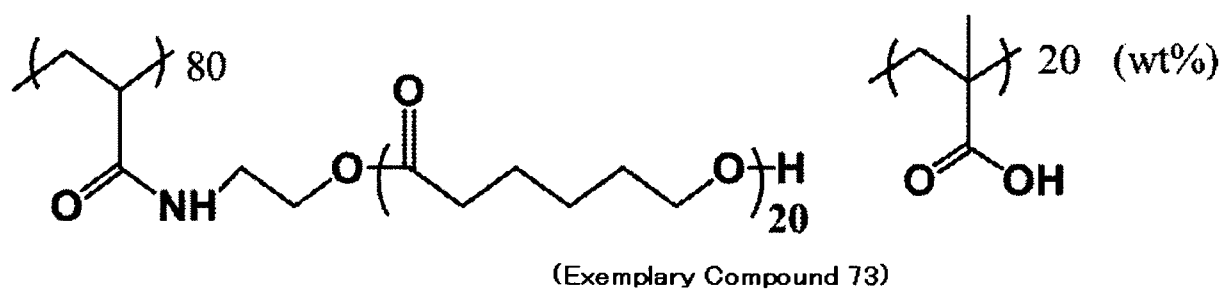
[0089]



[0090]



[0091]



[0092] As the dispersant in the invention, a compound having a polyester chain such as Exemplary Compound 72 is preferably used.

[0093] The content of the dispersant used in the preparation of a pigment dispersion in the invention is preferably from 1% by mass to 90% by mass, and more preferably 3% by mass to 70% by mass, with respect to the total solid content mass of the colorant (including a black pigment and other colorants) in the pigment dispersion.

[0094] (B) *Polymerization Initiator*

The black polymerizable composition of the invention includes a polymerization initiator.

The polymerization initiator used in the polymerizable composition of the invention is not particularly limited as long as it is capable of initiating polymerization of a polymerizable compound by application of any one or both of light and heat, and may be appropriately selected according to the purposes. However, in the case of initiating polymerization by light, a polymerization initiator having photosensitivity to rays ranging from an ultraviolet ray region to a visible light is preferably used.

Furthermore, in the case of initiating polymerization by heat, an initiator that decomposes at 150°C to 250°C is preferably used.

[0095] The polymerization initiator used in the invention is preferably a compound having at least an aromatic group. Examples thereof include (bis)acylphosphine oxides or esters thereof, acetophenone compounds, α -aminoketone compounds, benzophenone compounds, benzoin ether compounds, ketal derivative compounds, thioxanthone compounds, oxime ester compounds, hexaarylbiimidazole compounds, trihalomethyl compounds, azo compounds, organic peroxides, a metallocene compound, onium salt compounds such as a diazonium compound, an iodonium compound, a sulfonium compound, or an azinium compound, organic boron salt compounds, and disulfone compounds.

From the viewpoint of sensitivity, oxime ester compounds, acetophenone compounds, acylphosphine oxide compounds, α -aminoketone compounds, trihalomethyl compounds, hexaarylbiimidazole compounds, and thiol compounds are preferable, and acylphosphine oxide compounds, oxime ester compounds, α -aminoketone compounds, and the like are more preferable.

Examples of the polymerization initiator preferably used in the invention are described below, but the invention is not limited thereto.

[0096] Specific examples of the acetophenone compound 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-methylthiophenyl)-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-methyl thiophenyl)-2-morpholinopropan-1-one. Among these, 2-methyl-1-

(4-methylthiophenyl)-2-morpholinopropan-1-one that is preferably used in the invention is available under the trade name of "IRGACURE 907" (manufactured by BASF).

[0097] More preferable examples of the trihalomethyl compound include an s-triazine derivative having at least one mono-, di-, or trihalogen-substituted methyl group bonded to an s-triazine ring. 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-(4-methoxynaphthyl)-4,6-bis(trichloromethyl)-s-triazine, 2-phenylthio-4,6-bis(trichloromethyl)-s-triazine, 2-benzyl thio-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.

[0098] Examples of the hexaarylbiimidazole compound include various compounds such as those described, for example, in Japanese Patent Application Publication (JP-B) No. 6-29285, U.S. Patent Nos. 3,479,185, 4,311,783, and 4,622,286. 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.

[0099] Examples of the oxime ester compound include compounds described in J. C. S. Perkin II (1979) 1653-1660, J. C. S. Perkin II (1979) 156-162, Journal of Photopolymer Science and Technology (1995) 202-232, JP-A No. 2000-66385, JP-A No. 2000-80068, and JP-T No. 2004-534797. Preferable examples of commercially-available products thereof include IRGACURE OXE 01 (1,2-octanedione,1-[4-(phenylthio)-2-(o-benzoyloxime)]), and IRGACURE OXE 02 (ethanone,1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-,1-(o-acetyloxime)), both of which are manufactured by BASF Corporation.

Moreover, cyclic oxime compounds described in JP-A Nos. 2007-231000 and 2007-322744 may also be suitably used.

[0100] Examples of the acylphosphine oxide compound include the compounds described in JP-A No. 5-345790 and the compounds described in paragraph [0027] of JP-A No. 6-298818. Specific example thereof include bis(2,4,6-trimethylbenzoyl)isobutylphosphine oxide, bis(2,6-dimethoxybenzoyl)-n-butylphosphine oxide, and 2,6-dimethoxybenzoyl-2,4,6-trimethylbenzoyl-n-butylphosphine oxide. Further, preferable examples of commercially-available products thereof include DAROCURE TPO (trade name, manufactured by BASF Corporation) that is 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide.

[0101] Examples of the α -aminoketone compound include 2-(dimethylamino)-2-[(4-methylphenyl)methyl]-1-[4-(4-morpholinyl)phenyl]-1-butanone, which is available under the trade name of "IRGACURE 379 (manufactured by BASF Corporation)".

[0102] The polymerization initiators may be used singly or in combination of two or more kinds thereof.

The content of the polymerization initiator in the black polymerizable composition of the invention is preferably from 0.01% by mass to 30% by mass, more preferably from 0.1% by mass to 20% by mass, and particularly preferably from 0.1% by mass to 15% by mass, with respect to the total solid content of the black polymerizable composition.

[0103] *(C) Polymerizable Compound*

The black polymerizable composition of the invention includes a polymerizable compound.

As the (C) polymerizable compound, a compound which has at least one addition-polymerizable ethylenically unsaturated group and has a boiling point of 100°C or higher under the normal pressure is preferably used.

[0104] Examples of the compound having at least one addition-polymerizable ethylenically unsaturated group and a boiling point of 100°C or higher under the normal pressure include monofunctional acrylates and methacrylates such as polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, or phenoxyethyl (meth)acrylate; polyethylene glycol di(meth)acrylate, trimethylolethane tri(meth)acrylate, neopentyl glycol di(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, hexanediol (meth)acrylate, trimethylolpropane tri(acryloyloxypropyl)ether, tri(acryloyloxyethyl)isocyanurate, compounds obtained by addition of ethylene oxide or propylene oxide to a polyfunctional alcohol such as glycerol or trimethylolethane, followed by (meth)acrylation thereof, compounds obtained by poly(meth)acrylation of pentaerythritol or dipentaerythritol, urethane acrylates described in JP-B Nos. 48-41708, 50-6034, and JP-A No. 51-37193, polyester acrylates described in JP-A No. 48-64183, and JP-B Nos. 49-43191 and 52-30490, and epoxy acrylates produced by a

reaction between epoxy resins and (meth)acrylic acids.

Moreover, the compounds disclosed as photocurable monomers and oligomers in Journal of the Adhesion Society of Japan, Vol. 20, No. 7, pp. 300 to 308 may also be used.

[0105] Furthermore, the compounds obtained by addition of ethylene oxide or propylene oxide to the above-mentioned polyfunctional alcohol, followed by (meth)acrylation thereof, which are described in JP-A No. 10-62986 as the compounds represented by General Formulae (1) and (2) together with the specific examples thereof, may also be used.

[0106] In particular, dipentaerythritol penta(meth)acrylate, dipentaerythritol hexa(meth)acrylate, and compounds in which acryloyl groups thereof are bound via an ethylene glycol or propylene glycol residue, are preferable. Oligomers of these compounds may be used.

Furthermore, urethane acrylates as described in JP-B No. 48-41708, JP-A No. 51-37193, and JP-B Nos. 2-32293 and 2-16765, and urethane compounds having ethylene oxide skeletons as described in JP-B Nos. 58-49860, 56-17654, 62-39417, and 62-39418 are also preferable. Further, by the use of the addition-polymerizable compounds having an amino or sulfide structure in the molecule thereof described in JP-A Nos. 63-277653, 63-260909, and 1-105238, a black polymerizable composition having an extremely high photosensitive speed may be obtained. Examples of commercially-available product thereof include urethane oligomers UAS-10 and UAB-140 (both trade names, manufactured by Sanyo-Kokusaku Pulp Co., Ltd.), UA-7200 (trade name, manufactured by Shin-Nakamura Chemical Co., Ltd.), DPHA-40H (trade name, manufactured by Nippon Kayaku Co., Ltd.), UA-306H, UA-306T, UA-306I, AH-600, T-600, and AI-600 (trade names, manufactured by Kyoeisha Chemical Co., Ltd.), and KAYARAD DPCA-20, KAYARAD DPCA-30, KAYARAD DPCA-60, and KAYARAD DPCA-120 (trade name, manufactured by Nippon Kayaku Co., Ltd.).

In addition, ethylenically unsaturated compounds having an acid group are also preferable. 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 (both trade names, manufactured by Toagosei Co., Ltd.).

[0107] Moreover, succinic acid-modified monomers of dipentaerythritol hexaacrylate or dipentaerythritol pentaacrylate, pentaerythritol triacrylate, and the like are also preferable.

As the polymerizable compound used in the invention, a tetrafunctional or higher functional acrylate compound is more preferable.

[0108] The polymerizable compounds may be used singly or in combination of two or more kinds thereof. The content of the polymerizable compound in the black polymerizable composition is not particularly limited as long as a sufficient curing reaction is performed, but

it is preferably 3% by mass to 55% by mass, and more preferably 10% by mass to 50% by mass, with respect to 100 parts by mass of the total solid content.

[0109] *(E) Other Additives*

The black polymerizable composition of the invention may further contain various additives according to the purposes, in addition to the essential components of (A) to (D) and the pigment dispersant mentioned above.

(E-1) Binder polymer having different structure from that of (D) component

In the black polymerizable composition, an additional binder polymer (hereinafter also simply referred to as the (E-1) additional binder polymer) having a structure different from that of the (D) component may further be use as desired, for the purpose of improvement of film characteristics or the like, within a range in which the characteristics of the black polymerizable composition of the invention are not impaired.

[0110] Here, a linear organic polymer is preferably used as the binder polymer. As the “linear organic polymer”, any known linear organic polymer may be used. Preferably, a linear organic polymer which is soluble or swellable in water or weakly alkaline water is selected for enabling development in water or development in weakly alkaline water. The linear organic polymer is selected not only as a coating film-forming agent but also depending on the type of a developer such as water, weakly alkaline water, or an organic solvent.

[0111] For example, water development is feasible when a water-soluble organic polymer is used. Examples of such liner organic polymers include radical polymers each having a carboxylic acid group in the side chain, such as those described in, for example, JP-A No. 59-44615, JP-B Nos. 54-34327, 58-12577, and 54-25957, and JP-A Nos. 54-92723, 59-53836, and 59-71048, that is, a resin obtained by homopolymerization or copolymerization of a monomer having a carboxyl group, a resin obtained by homopolymerization or copolymerization of a monomer having an acid anhydride and then hydrolyzing, half-esterifying or half-amidating the acid anhydride unit, and epoxy acrylate obtained by modifying epoxy resin with unsaturated monocarboxylic acid and acid anhydride. Examples of the monomer having a carboxyl group include acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, and 4-carboxystyrene, and examples of the monomer having an acid anhydride include maleic anhydride.

Similarly, acidic cellulose derivatives having a carboxylic acid group in the side chain may be used. Moreover, those obtained by adding a cyclic acid anhydride to a polymer having a hydroxyl group, and the like are useful.

[0112] Furthermore, urethane binder polymers containing an acid group, as described in JP-B Nos. 7-12004, 7-120041, 7-120042, and 8-12424, JP-A Nos. 63-287944, 63-287947, and 1-

271741, Japanese Patent Application No. 10-116232, and the like, are advantageous in terms of low-exposure suitability because they have extremely high strength.

Acetal-modified polyvinyl alcohol binder polymers having an acid group as described in European Patent (EP) Nos. 993966 and 1204000, JP-A No. 2001-318463, and the like are preferable owing to the excellent balance between film strength and developability.

As other water-soluble linear organic polymers, polyvinyl pyrrolidone, polyethylene oxide, or the like is useful. To increase the strength of a cured film, alcohol-soluble nylon, polyethers of 2,2-bis-(4-hydroxyphenyl)-propane and epichlorohydrin, and the like are also useful.

The content of the coexisting additional binder polymer with respect to the total solid content of the black polymerizable composition of the invention is preferably from 0.1% by mass to 7.0% by mass, and from the viewpoints of compatibility between inhibition of pattern peeling and inhibition of development residues, it is more preferably from 0.3% by mass to 6.0% by mass, and even more preferably from 1.0% by mass to 5.0% by mass.

[0113] *(E-2) Colorants other than (A) components*

In the invention, other colorants that are different from the (A) component may additionally be used, if necessary, in order to exhibit a desired light-shielding property.

Examples of organic pigment which may be used as a colorant together with the (A) component include pigments described in paragraphs [0030] to [0044] of JP-A No. 2008-224982, C. I. Pigment Green 58, and a colorant obtained by changing a Cl substituent of C. I. Pigment Blue 79 to an OH substituent. In particular, examples of pigment which may be preferably used include:

C. I. Pigment Yellow 11, 24, 108, 109, 110, 138, 139, 150, 151, 154, 167, 180, and 185;

C. I. Pigment Orange 36;

C. I. Pigment Red 122, 150, 171, 175, 177, 209, 224, 242, 254, and 255;

C. I. Pigment Violet 19, 23, 29, and 32;

C. I. Pigment Blue 15:1, 15:3, 15:6, 16, 22, 60, and 66;

C. I. Pigment Green 7, 36, 37, and 58; and

C. I. Pigment Black 1.

However, the colorants which may be used together with the (A) component are not limited thereto.

[0114] The dye which may be used as the additional colorant is not particularly limited, and any dye selected from known dyes may be used. Example of dyes include dyes disclosed in JP-A No. 64-90403, JP-A No. 64-91102, JP-A No. 1-94301, JP-A No. 6-11614, Japanese

Patent No. 2592207, US Patent No. 4,808,501, US Patent No. 5,667,920, US Patent No. 5,059,500, JP-A No. 5-333207, JP-A No. 6-35183, JP-A No. 6-51115, JP-A No. 6-194828, JP-A No. 8-211599, JP-A No. 4-249549, JP-A No. 10-123316, JP-A No. 11-302283, JP-A No. 7-286107, JP-A No. 2001-4823, JP-A No. 8-15522, JP-A No. 8-29771, JP-A No. 8-146215, JP-A No. 11-343437, JP-A No. 8-62416, JP-A No. 2002-14220, JP-A No. 2002-14221, JP-A No. 2002-14222, JP-A No. 2002-14223, JP-A No. 8-302224, JP-A No. 8-73758, JP-A No. 8-179120, and JP-A No. 8-151531.

Furthermore, dyes having chemical structures of a pyrazole azo dye, an anilinoazo dye, a triphenylmethane dye, an anthraquinone dye, an anthrapyridone dye, a benzylidene dye, an oxonol dye, a pyrazoletriazoleazo dye, a pyridoneazo dye, a cyanine dye, a phenothiazine dye, a pyrrolopyrazoleazomethine dye, a xanthene dye, a phthalocyanine dye, a benzopyran dye, an indigo dye, or the like may also be used.

[0115] *(E-3) Organic Solvent*

To the black polymerizable composition of the invention, a solvent may be added. The organic solvent is not basically particularly limited as long as solubility of each component and coating property of the black polymerizable composition are satisfied, but is preferably selected in consideration of an ultraviolet ray absorbent to be used, the solubility of the binder, coating property, and safety. Further, in order to prepare the black polymerizable composition in the invention, at least two kinds of organic solvents are preferably contained.

[0116] Preferable examples of the organic solvent include:

esters such as ethyl acetate, n-butyl acetate, isobutyl acetate, amyl formate, isoamyl acetate, isobutyl acetate, butyl propionate, isopropyl butyrate, ethyl butyrate, butyl butyrate, methyl lactate, ethyl lactate, alkyl oxyacetate (e.g., methyl oxyacetate, ethyl oxyacetate, butyl oxyacetate (for example, methyl methoxyacetate, ethyl methoxyacetate, butyl methoxyacetate, methyl ethoxyacetate, and ethyl ethoxyacetate)), 3-oxypropionate alkyl esters (e.g., methyl 3-oxypropionate and ethyl 3-oxy propanoate (for example, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, methyl 3-ethoxypropionate, and ethyl 3-ethoxypropionate)), 2-oxypropionate alkyl esters (e.g., methyl 2-oxypropionate, ethyl 2-oxypropionate, and propyl 2-oxypropionate (for example, methyl 2-methoxypropionate, ethyl 2-methoxypropionate, propyl 2-methoxypropionate, methyl 2-ethoxypropionate, and ethyl 2-ethoxypropionate)), methyl 2-oxy-2-methylpropionate and ethyl 2-oxy-2-methylpropionate (e.g., methyl 2-methoxy-2-methylpropionate and ethyl 2-ethoxy-2-methylpropionate), methyl pyruvate, ethyl pyruvate, propyl pyruvate, methyl acetoacetate, ethyl acetoacetate, methyl 2-oxobutanoate, ethyl 2-oxobutanoate;

ethers such as diethylene glycol dimethyl ether, tetrahydrofuran, ethylene glycol

monomethyl ether, ethylene glycol monoethyl ether, methyl cellosolve acetate, ethyl cellosolve acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, or propylene glycol monopropyl ether acetate;

ketones such as methyl ethyl ketone, cyclohexanone, 2-heptanone, or 3-heptanone; and

aromatic hydrocarbons such as toluene or xylene.

[0117] Two or more kinds of these organic solvents are preferably mixed from the viewpoints of the solubility of an ultraviolet ray absorbent and an alkali-soluble resin, improvement of the profile of a coated surface, and the like. In such a case, it is particularly preferable to use a mixed solution including two or more selected from methyl 3-ethoxypropionate, ethyl 3-ethoxypropionate, ethyl cellosolve acetate, ethyl lactate, diethylene glycol dimethyl ether, butyl acetate, methyl 3-methoxypropionate, 2-heptanone, cyclohexanone, ethyl carbitol acetate, butyl carbitol acetate, propylene glycol methyl ether, and propylene glycol methyl ether acetate.

[0118] The content of the organic solvent in the black polymerizable composition is preferably an amount such that the total solid concentration of the composition is 5% by mass to 80% by mass, more preferably 5% by mass to 60% by mass, and particularly preferably 10% by mass to 50% by mass, from the viewpoints of coating property.

[0119] *(E-4) Surfactant*

From the viewpoint of improving the coating property, any one of various surfactants may be added to the black polymerizable composition of the invention. As the surfactant, various surfactants such as a fluorine-containing surfactant (fluorosurfactant), a nonionic surfactant, a cationic surfactant, an anionic surfactant, or a silicone surfactant may be used.

[0120] Particularly, when the black polymerizable composition of the invention contains a fluorosurfactant, the liquid characteristics (particularly, flowability) of a coating liquid prepared using the black polymerizable composition is further improved, whereby the uniformity or film-forming property is further improved.

In other words, when a film is formed using a coating liquid which contains a black polymerizable composition containing a fluorosurfactant, the interfacial tension between a surface to be coated and the coating liquid is lowered, and wettability to the surface to be coated is improved, leading to improvement in coatability of the coating liquid to the surface to be coated. For this reason, even when a thin film of several μm is formed using a small amount of the coating liquid, formation of a film having a uniform film thickness with small

thickness differentiation is preferably carried out.

[0121] The fluorine content in the fluorosurfactant is preferably from 3% by mass to 40% by mass, more preferably from 5% by mass to 30% by mass, and particularly preferably from 7% by mass to 25% by mass. A fluorosurfactant having a fluorine content ratio within these ranges is effective in terms of uniformity of the thickness of the coated film and the liquid-saving property, and the solubility in the colored photosensitive composition is also good.

[0122] Examples of the fluorosurfactant 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, and MEGAFAC F781 (all trade names, manufactured by DIC Corporation), FLUORAD FC430, FLUORAD FC431, and FLUORAD FC171 (all trade names, manufactured by Sumitomo 3M Limited), 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, and SURFLON KH-40 (all trade names, manufactured by Asahi Glass Co., Ltd.).

[0123] Specific examples of the nonionic surfactant include glycerol, trimethylolpropane, trimethylolethane, and ethoxylates and propoxylates thereof (for example, glycerol propoxylate, and glycerin ethoxylate), polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene nonyl phenyl ether, polyethylene glycol dilaurate, polyethylene glycol distearate, sorbitan fatty acid ester (such as PLURONIC L10, L31, L61, L62, 10R5, 17R2, and 25R2, TETRONIC 304, 701, 704, 901, 904, or 150R1 (trade names, manufactured by BASF Corporation)), and SOLFPERSE 20000 (trade name, manufactured by The Lubrizol Corporation, Japan).

[0124] Specific examples of the cationic surfactant include a phthalocyanine derivative (trade name: EFKA-745, manufactured by Morishita & Co., Ltd.), an organosiloxane polymer KP341 (manufactured by Shin-Etsu Chemical Co., Ltd.), a (meth)acrylic (co)polymer POLYFLOW No. 75, 90, and 95 (manufactured by Kyoeisha Chemical Co., Ltd.), and W001 (trade name, manufactured by Yusho Co., Ltd.).

[0125] Specific examples of the anionic surfactant include W004, W005, and W017 (trade names, manufactured by Yusho Co., Ltd.).

[0126] 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, all manufactured by Dow Corning Toray Co., Ltd.), TSF-4440, TSF-4300, TSF-4445, TSF-4460, and TSF-4452 (trade names, all manufactured by Momentive Performance Materials Inc.), KP341, KF6001, and KF6002 (trade names, all manufactured by Shin-Etsu Chemical Co., Ltd.), and BYK307, BYK323, and BYK330 (trade names, manufactured by BYK Chemie).

The surfactants may be used singly or in combination of two or more kinds thereof.

The amount of the surfactant to be added is preferably 0.001% by mass to 2.0% by mass, and more preferably 0.005% by mass to 1.0% by mass, with respect to the total mass of the black polymerizable composition.

[0127] *(E-5) Sensitizer*

The black polymerizable composition may further contain a sensitizer for the purpose of improving the radical generation efficiency of the polymerization initiator, and attaining a longer wavelength at the photosensitive wavelengths.

As the sensitizer used in the invention, a sensitizer that sensitizes the polymerization initiator used therewith by an electron transfer mechanism or an energy transfer mechanism is preferable.

Preferable examples of the sensitizer include the compounds described in paragraphs [0085] to [0098] of JP-A No. 2008-214395.

The content of the sensitizer is preferably in the range of from 0.1% by mass to 30% by mass, and more preferably in the range of from 1% by mass to 20% by mass, and even more preferably in the range of from 2% by mass to 15% by mass, with respect to the total solid mass of the black polymerizable composition, from the viewpoints of sensitivity and storage stability.

[0128] *(E-6) Polymerization Inhibitor*

It is preferable to add a small amount of a polymerization inhibitor to the black polymerizable composition so as to prevent the undesirable heat polymerization of the polymerizable compound during the preparation or storage of the composition. As the polymerization inhibitor, a known heat polymerization inhibitor may be used. Examples thereof include hydroquinone, p-methoxyphenol, di-t-butyl-p-cresol, pyrogallol, t-butylcatechol, benzoquinone, 4,4'-thiobis(3-methyl-6-t-butylphenol), 2,2'-methylenebis(4-methyl-6-t-butylphenol), and cerous salts of N-nitrosophenyl hydroxylamine.

The amount of the heat polymerization inhibitor to be added is preferably about 0.01% by mass to about 5% by weight, with respect to the total solid content of the black polymerizable composition.

Further, a higher fatty acid or derivative thereof such as behenic acid or a behenic

acid amide may be added so as to be present at the surface of the coating film during the process of drying after the coating, so that the polymerization inhibition due to oxygen is inhibited. The amount of the higher fatty acid or derivative thereof to be added is preferably about 0.5% by mass to about 10% by mass with respect to the total composition.

[0129] *(E-7) Adhesion Improving Agent*

An adhesion improving agent may be added to the black polymerizable composition of the invention in order to improve adhesiveness to the surface of a hard material such as a support. Examples of the adhesion improving agent include a silane coupling agent and a titanium coupling agent.

Preferable examples of the silane coupling agent include γ -methacryloxypropyl trimethoxy silane, γ -methacryloxypropyl triethoxy silane, γ -acryloxypropyl trimethoxy silane, γ -acryloxypropyl triethoxy silane, γ -mercaptopropyl trimethoxy silane, γ -aminopropyl triethoxy silane, phenyl trimethoxy silane, and 3-methacryloxypropyl dimethoxymethyl silane. More preferable examples include 3-methacryloxypropyl dimethoxymethyl silane and γ -methacryloxypropyl trimethoxy silane.

The amount of the adhesion improving agent to be added is preferably from 0.5% by mass to 30% by mass, and more preferably from 0.7% by mass to 20% by mass, with respect to the total solid content of the black polymerizable composition of the invention.

In particular, when the resist (i.e., the black polymerizable composition) of the present invention is used for forming a lens on a glass substrate, it is preferable to add an adhesion improving agent to the resist from the viewpoint of the improvement of sensitivity.

[0130] *(E-8) Other Additives*

The black polymerizable composition of the invention may further contain a co-sensitizer for the purpose of, for example, further improving the sensitivity of a sensitizing colorant or an initiator to actinic radiation, or prevent polymerization inhibition of a photopolymerizable compound caused by oxygen. In addition, in order to improve the physical properties of the cured coating film, known additives such as a surfactant, a diluent, a plasticizer, or an oil-sensitizing agent may be added, if necessary.

[0131] The black polymerizable composition of the invention contains at least (A) the black material (preferably, a pigment dispersion composition containing a pigment dispersant), (B) the polymerization initiator, (C) the polymerizable compound, and (D) the alkali-soluble binder polymer, which are mentioned above, and, if necessary, may further contain any one of various additives and (E-3) an organic solvent, and may be prepared by mixing these components and, if necessary, additives such as a surfactant.

[0132] When the black polymerizable composition of the invention has such a configuration,

a light-shielding film having an excellent alkali developer resistance is formed. For this reason, the black polymerizable composition is useful for forming the light-shielding region of a wafer level lens.

Further, for forming a light-shielding film, it is preferable to apply the black polymerizable composition onto a solid surface by spray-coating, as described below.

Therefore, from the viewpoints of prevention of liquid drainage when the black polymerizable composition is coated onto a curved surface, the total solid content in the black polymerizable composition is preferably from 20% by mass to 35% by mass, more preferably from 21% by mass to 33% by mass, and most preferably from 25% by mass to 30% by mass.

[0133] *Wafer Level Lens*

The wafer level lens of the invention may include a light-shielding film (i.e., a black layer) formed from the black polymerizable composition of the invention.

Hereinbelow, the wafer level lens of the invention will be described.

[0134] Fig. 1 is a plain view showing an example of the configuration of a wafer level lens array having plural wafer level lenses.

As shown in Fig. 1, the wafer level lens array includes a substrate 10, and lenses 12 arranged on the substrate 10. In Fig. 1, the plural lenses 12 are two-dimensionally arranged with respect to the substrate 10, but they may also be one-dimensionally arranged.

Fig. 2 is a cross-sectional view of the wafer level lens array shown in Fig. 1, which is taken along the line A-A.

As shown in Fig. 2, in the wafer level lens array, a light-shielding film 14 that prevents light transmission in regions other than the lenses 12 is formed among the plural lenses 12 arranged on the substrate 10.

The wafer level lens of the invention includes one lens 12 present on the substrate 10, and the light-shielding film 14 provided on the peripheral portion of the lens. The black curable composition of the invention is used in forming the light-shielding film 14, thereby forming a light-shielding region.

[0135] Hereinbelow, a configuration of the wafer level lens array, in which plural lenses 12 are arranged two-dimensionally with respect to the substrate 10, as shown Fig. 1, will be described by way of example.

[0136] The lens 12 is generally formed from the same material as that of the substrate 10, and may be integrally formed on the substrate 10 or may be formed as a separate structure and fixed on the substrate. Herein, an example of the wafer level lens of the invention is cited, but the wafer level lens of the invention is not limited thereto, and various embodiments such as one which has a multilayer structure or one which is separated into lens modules by dicing,

may be employed.

[0137] Examples of materials for forming the lens 12 include glass. There are various types of glass, and glass is preferably used as a material for a lens having high power because a glass having a high refractive index may be selected from various types of glass. Further, glass has advantages of excellent heat resistance and withstanding reflow-mounting on an imaging unit.

[0138] Examples of other materials for forming the lens 12 include resins. A resin has excellent workability, and is suitable in that the surface of the lens is formed easily and inexpensively using, for example, a mold or die.

[0139] The wafer level lens is preferably formed using an energy-curable resin. The energy-curable resin may be any of a resin capable of being cured by heating or a resin capable of being cured by irradiation of active energy rays (for example, heat application, ultraviolet ray radiation, or electron beam radiation).

Considering reflow-mounting of an imaging unit, a resin having a relatively high softening point, for example, of 200°C or higher, is preferable, and a resin having a softening point of 250°C or higher is more preferable.

The preferable resin as the lens material will be described below.

[0140] Examples of an ultraviolet curable resin include an ultraviolet curable silicone resin, an ultraviolet curable epoxy resin, and an ultraviolet curable acryl resin. The epoxy resin which can be used in the invention has a linear expansion coefficient of from 40 to 80 [$10^{-6}/\text{K}$] and has a refractive index of from 1.50 to 1.70, and preferably from 1.50 to 1.65.

[0141] Examples of a thermosetting resin include a thermosetting silicone resin, a thermosetting epoxy resin, a thermosetting phenol resin, and a thermosetting acryl resin. For example, the silicon resin which can be used has a linear expansion coefficient of from 30 to 160 [$10^{-6}/\text{K}$] and has a refractive index of from 1.40 to 1.55. For example, the epoxy resin which can be used has a linear expansion coefficient of from 40 to 80 [$10^{-6}/\text{K}$] and has a refractive index of from 1.50 to 1.70, and preferably from 1.50 to 1.65. The phenol resin which can be used has a linear expansion coefficient of from 30 to 70 [$10^{-6}/\text{K}$] and has a refractive index of from 1.50 to 1.70. The acryl resin which can be used has a linear expansion coefficient of from 20 to 60 [$10^{-6}/\text{K}$] and has a refractive index of from 1.40 to 1.60, and preferably from 1.50 to 1.60.

[0142] A commercially-available product may be used as the thermosetting resin. Specific examples thereof include SMX-7852 and SMX-7877 (both trade names, manufactured by Fuji Polymer Industries Co., Ltd.), IVSM-4500 (trade name, manufactured by Toshiba Corporation), and SR-7010 (trade name, manufactured by Dow Corning Toray Co., Ltd.).

[0143] Examples of a thermoplastic resin include a polycarbonate resin, a polysulfone resin, and a polyester sulfone resin. The polycarbonate resin which can be used has a linear expansion coefficient of from 60 to 70 [$10^{-6}/\text{K}$] and has a refractive index of from 1.40 to 1.70, and preferably from 1.50 to 1.65. The polysulfone resin which can be used has a linear expansion coefficient of from 15 to 60 [$10^{-6}/\text{K}$] and has a refractive index of 1.63. The polyether sulfone resin which can be used has a linear expansion coefficient of from 20 to 60 [$10^{-6}/\text{K}$] and has a refractive index of 1.65.

[0144] Furthermore, optical glass generally has a linear expansion coefficient of from 4.9 to 14.3 [$10^{-6}/\text{K}$] at 20°C and has a refractive index of from 1.4 to 2.1 at wavelength of 589.3 nm. In addition, quartz glass has a linear expansion coefficient of from 0.1 to 0.5 [$10^{-6}/\text{K}$] and has a refractive index of about 1.45.

[0145] It is preferable that the curable resin composition capable of being used for forming a lens has a suitable flowability before curing, from the viewpoints of formability such as transfer suitability of mold shape. Specifically, it is preferable that the curable resin composition be liquid at the normal temperature and have a viscosity of from about 1,000 mPa·s to about 50,000 mPa·s.

[0146] On the other hand, it is preferable that the curable resin composition capable of being used for forming a lens have a heat resistance so that it does not suffer from heat deformation through a reflow process after curing. From these viewpoints, a glass transition temperature of the cured material is preferably 200°C or higher, more preferably 250°C or higher and particularly preferably 300°C or higher. In order to impart such a high heat resistance to the resin composition, it is necessary to suppress mobility at a molecular level. Examples of an effective method therefor include (1) increasing a crosslinking density per unit volume, (2) using a resin having a rigid cyclic structure (for example, a resin having an alicyclic structure such as cyclohexane, norbornane, or tetracyclododecane, an aromatic structure such as benzene or naphthalene, a cardo structure such as 9,9'-biphenyl fluorene, or a spiro structure such as spirobiindane, specifically, for example, resins described in JP-A Nos. 9-137043, 10-67970, 2003-55316, 2007-334018, and 2007-238883, and the like), and (3) homogeneously dispersing a high T_g material such as an inorganic fine particle (for example, those described in JP-A Nos. 5-209027 and 10-298265). These methods may be used singly or in combination of plural kinds, and are preferably adjusted in a range not impairing other properties such as flowability, a shrinkage ratio, or a refractive index.

[0147] From the viewpoints of the degree of precision of shape transfer, a curable resin composition which exhibits a low volume shrinkage ratio by a curing reaction is preferable. The curing shrinkage ratio of the resin composition used in the invention is preferably 10% or

less, more preferably 5% or less, and particularly preferably 3% or less.

[0148] Examples of the resin composition having a low curable shrinkage ratio include the following (1) to (6):

(1) a resin composition containing a high molecular weight curing agent (for example, prepolymer) (for example, a composition as described in JP-A No. 2001-19740, JP-A No. 2004-302293, and JP-A No. 2007-211247), in which the number average molecular weight of the high molecular weight curing agent is preferably in a range of from 200 to 100,000, more preferably in a range of from 500 to 50,000 and particularly preferably in a range of from 1,000 to 20,000; and a value obtained by calculating the number average molecular weight of the curing agent/the number of curing reactive groups in the curing agent is preferably in a range of from 50 to 10,000, more preferably in a range of from 100 to 5,000 and particularly preferably in a range of from 200 to 3,000;

(2) a resin composition containing a non-reactive material (for example, an organic fine particle, an inorganic fine particle, or a non-reactive resin) (for example, the composition as described in JP-A No. 6-298883, JP-A No. 2001-247793 and JP-A No. 2006-225434);

(3) a resin composition containing a relatively low shrinkage-crosslinking reactive group (for example, a ring-opening polymerizable group such as an epoxy group (for example, one described in JP-A No. 2004-210932), an oxetanyl group (for example, one described in JP-A No. 8-134405), an episulfide group (for example, one described in JP-A No. 2002-105110), a cyclic carbonate group (for example, one described in JP-A No. 7-62065), an ene/thiol curing group (for example, one described in JP-A No. 2003-20334), a hydrosilylation curing group (for example, one described in JP-A No. 2005-15666);

(4) a resin composition containing a resin having a rigid skeleton (for example, fluorene, adamantane, or isophorone) (for example, one described in JP-A No. 9-137043);

(5) a resin composition which contains two kinds of monomers having different polymerizable groups and forms an interpenetrating-network structure (i.e., IPN structure) (for example, one described in JP-A No. 2006-131868); and

(6) a resin composition containing an expansible material (for example, composition in described JP-A No. 2004-2719 and JP-A No. 2008-238417). Further, it is preferable to use a combination of two or more of the curing shrinkage-reducing means (for example, a resin composition which contains a prepolymer containing a ring-opening polymerizable group and fine particles), from the viewpoint of optimization of physical properties.

[0149] For forming the wafer level lens of the invention, two kinds or more of resin compositions having different high and low Abbe numbers, respectively, are preferred.

In a resin having a relatively high Abbe number, the Abbe number (v_d) is preferably

50 or more, more preferably 55 or more, and particularly preferably 60 or more. The refractive index (nd) of the resin is preferably 1.52 or more, more preferably 1.55 or more and particularly preferably 1.57 or more.

The resin is preferably an aliphatic resin, and is more preferably a resin having an alicyclic structure (for example, a resin having a cyclic structure such as cyclohexane, norbornane, adamantane, tricyclodecane, or tetracyclododecane, specifically for example, resins described in JP-A No. 10-152551, JP-A No. 2002-212500, JP-A No. 2003-20334, JP-A No. 2004-210932, JP-A No. 2006-199790, JP-A No. 2007-2144, JP-A No. 2007-284650, and JP-A No. 2008-105999).

[0150] In a resin having a relatively low Abbe number, the Abbe number (vd) is preferably 30 or less, more preferably 25 or less, and particularly preferably 20 or less. The refractive index (nd) of the resin is preferably 1.60 or more, more preferably 1.63 or more and particularly preferably 1.65 or more.

The resin is preferably a resin having an aromatic structure, and more preferably, for example, a resin containing a structure of 9,9'-diarylfuorene, naphthalene, benzothiazole, benzotriazole, or the like (specifically, for example, resins described in JP-A No. 60-38411, JP-A No. 10-67977, JP-A No. 2002-47335, JP-A No. 2003-238884, JP-A No. 2004-83855, JP-A No. 2005-325331, JP-A No. 2007-238883, WO 2006/095610, and Japanese Patent No. 2537540).

[0151] In the resin composition used for forming a wafer level lens, it is preferable to use an organic or inorganic composite material containing inorganic fine particles dispersed in a matrix, from the viewpoints of increasing a refractive index or adjusting the Abbe number.

Examples of the inorganic fine particles in the organic or inorganic composite material include oxide fine particles, sulfide fine particles, selenide fine particles, and telluride fine particles. Specific examples thereof include fine particles of zirconium oxide, titanium oxide, zinc oxide, tin oxide, niobium oxide, cerium oxide, aluminum oxide, lanthanum oxide, yttrium oxide, zinc sulfide or the like.

[0152] The inorganic fine particles may be used singly or in combination of two or more kinds thereof. Further, The inorganic fine particles may be made from a composite of plural components.

In order to reduce, for example, photocatalytic activity and water absorption, the inorganic fine particles may be doped with a heterogeneous metal, or a surface layer thereof may be coated with a heterogeneous metal oxide such as silica or alumina, or the surface thereof may be modified using a silane coupling agent, a titanate coupling agent, an organic acid (for example, carboxylic acids, sulfonic acids, phosphoric acids, and phosphonic acids), a

dispersant having an organic acid group, or the like.

The number average primary particle size of the inorganic fine particles may be generally from about 1 nm to 1,000 nm. When the particle size is too small, there are cases where the physical properties are changed. When the particle size is too large, the effect of Rayleigh scattering is pronounced. In this regard, the number average primary particle size is preferably from 1 nm to 15 nm, more preferably from 2 nm to 10 nm and particularly preferably from 3 nm to 7 nm. Further, a narrower particle size distribution of the inorganic fine particles is preferable. The monodispersed particle has various definitions, and for example, the defined range of values as described in JP-A No. 2006-160992 corresponds to a preferable particle size distribution range.

The number average primary particle size described above may be measured using, for example, an X-ray diffraction (XRD) apparatus, a transmission electron microscope (TEM), or the like.

[0153] The refractive index of the inorganic fine particles at 22°C and at a wavelength of 589.3 nm is preferably from 1.90 to 3.00, more preferably from 1.90 to 2.70, and particularly preferably from 2.00 to 2.70.

[0154] The content of the inorganic fine particles in the organic-inorganic composite materials is 5% by mass or more, more preferably 10% by mass to 70% by mass, and particularly preferably 30% by mass to 60% by mass, with respect to the resin that is a matrix for the inorganic fine particles, from the viewpoints of transparency and a higher refractive index.

[0155] Examples of the resin serving as the matrix used in the organic-inorganic composite material include the ultraviolet curable resin, thermosetting resin, thermoplastic resin having a relatively high Abbe number, and resin having a relatively low Abbe number, which are described above as wafer level lens materials. Further, examples of the resin include a resin having a refractive index higher than 1.60, such as those described in JP-A No. 2007-93893, a block copolymer consisting of a hydrophobic segment and a hydrophilic segment, such as those described in JP-A No. 2007-211164, a resin having a functional group capable of forming an arbitrary chemical bond with an inorganic fine particle, at an end or side chain of a polymer, such as those described in JP-A No. 2007-238929, Japanese Patent Application Nos. 2008-12645, 2008-208427, 2008-229629, and 2008-219952, and a thermoplastic resin described in Japanese Patent Application Nos. 2008-197054 and 2008-198878.

Further, additives such as a plasticizer or a dispersant may be added to the organic-inorganic composite material, if necessary.

[0156] In this regard, preferable combinations of the resin as a matrix and the inorganic fine

particles are as follows.

That is, when the resin having a relatively high Abbe number as described above is used as a matrix, it is preferable that fine particles of lanthanum oxide, aluminum oxide, zirconium oxide, or the like as the inorganic fine particles be dispersed in the resin. When the resin having a relatively low Abbe number is used as a matrix, it is preferable that fine particles of titanium oxide, tin oxide, zirconium oxide, or the like as the inorganic fine particles be dispersed in the resin.

[0157] In order to homogeneously disperse the inorganic fine particles, it is preferable to appropriately use, for example, a dispersant containing a functional group having a reactivity to the resin monomer for forming a matrix (for example, dispersants described in the Examples section of JP-A No. 2007-238884, and the like), a block copolymer formed from a hydrophobic segment and a hydrophilic segment (for example, those described in JP-A No. 2007-211164) or a resin having a functional group capable of forming arbitrary chemical bonds with inorganic fine particles in an end or a side chain of a high molecular (for example, those described in JP-A Nos. 2007-238929 and 2007-238930, and the like).

[0158] The resin composition used for forming a wafer level lens in the invention may be suitably blended with an additive such as a known releasing agent such as a silicon compound, a fluorine-containing compound, or a long-chain alkyl group-containing compound; or an antioxidant such as hindered phenol.

[0159] The resin composition used for forming a wafer level lens in the invention may be blended with a curing catalyst or initiator, if necessary. Specific examples thereof include a compound that promotes a curing reaction (radical polymerization or ion polymerization) by action of heat or active energy rays, as described in paragraphs [0065] to [0066] of JP-A No. 2005-92099. The amount of the curing reaction promoter to be added may vary depending on the type of a catalyst or initiator, or the type of a curing reactive moiety, and thus the amount cannot be unconditionally set. However, the amount is preferably from about 0.1% by mass to 15% by mass, and more preferably from about 0.5% by mass to 5% by mass, with respect to the total solid content of the resin composition.

[0160] The resin composition used in producing the wafer level lens of the invention may be produced by appropriately blending the above-mentioned components. At this time, when components other than a liquid lower molecular weight monomer (reactive diluent) are dissolvable in the monomer, no separate solvent is required to be added, while in a case in which the components do not dissolve in the liquid lower molecular weight monomer, respective components may be dissolved using a solvent, thereby preparing a resin composition. The solvent which may be used in the resin composition is not specifically

limited, and may be selected suitably as long as no precipitation is generated in the resultant composition, and homogeneous dissolution and dispersion are achieved. Specific examples of the solvent include ketones (for example, acetone, methyl ethyl ketone, and methyl isobutyl ketone), esters (for example, ethyl acetate and butyl acetate), ethers (for example, tetrahydrofuran and 1,4-dioxane), alcohols (for example, methanol, ethanol, isopropyl alcohol, butanol, and ethylene glycol), aromatic hydrocarbons (for example, toluene and xylene), and water. When the resin composition contains the solvent, it is preferred that the composition is cast on a substrate and/or a mold, and the solvent is dried, followed by carrying out a transfer operation by mold shape.

[0161] The substrate 10 may be formed from the same material as the molding material of the lens 12. Alternatively, the substrate 10 may be formed from a material different from the molding material of the lens 12 as long as the substrate 10 is formed from a material transparent with respect to visible light, such as a glass. In this case, it is preferred that the material for forming the substrate 10 has the same or substantially the same linear expansion coefficient as that of the material for forming the lens 12. In a case in which a linear expansion coefficient of the material for forming lens 12 is the same or substantially the same as that of the material for forming the substrate 10, distortion or breaking of the lens 12 during heating, which is caused owing to different linear expansion ratios, is suppressed in reflow mounting of the wafer level lens on an imaging unit.

[0162] Although not shown in Figs. 1 and 2, an infrared filter (IR filter) may be formed on the surface of the optical incidence side of the substrate 10.

[0163] Hereinbelow, with reference to Figs. 3 to 8C, specific description will be given to the configuration and production of a wafer level lens, by referring to a method of producing a wafer level lens array.

[0164] *Configuration and Production of Wafer Level Lens (1)*

Formation of Lens

First, with reference to Figs. 3 and 4A to 4C, a method for forming a lens 12 on a substrate 10 is described.

Here, Fig. 3 is a view showing the state of supplying a molding material (referred to as "M" in Fig. 3) that is a resin composition for forming a lens, onto a substrate 10.

Figs. 4A to 4C are schematic views showing the procedures of molding a lens 12 on a substrate 10 using a mold 60.

[0165] As shown in Fig. 3, the molding material M is applied dropwise, using a dispenser 50, onto regions of the substrate 10 on which the lenses 12 are to be formed. The molding material M in an amount necessary for forming one lens 12 is supplied to each of the regions

onto which the lenses are to be supplied.

[0166] After the molding material M is supplied to the substrate 10, the mold 60 for forming a lens 12 is disposed over the surface of the substrate 10, on which the molding material M has been supplied, as shown in Fig. 4A.

Here, plural concave portions 62 for transferring the shape of a lens 12 is provided in the mold 60 according to a desirable number of the lenses 12.

[0167] Subsequently, as shown in Fig. 4B, the mold 60 is pressed to the molding material M on the substrate 10, so that the molding material M is deformed according to the shape of the concave portions 62. Then, the molding material M is cured while the mold 60 is pressed to the molding material M, by irradiation of heat or ultraviolet light from the outside of the mold 60 when the molding material M is a thermosetting resin or an ultraviolet curable resin.

[0168] After the molding material M is cured, the substrate 10 and the lenses 12 are released from the mold 60 as shown in Fig. 4C.

[0169] *Formation of Light-shielding Film*

With reference to Figs. 5A to 5C, a method of forming a light-shielding film 14 in the peripheral portion of the lenses 12 will be described.

Herein, Figs. 5A to 5C are schematic cross-sectional views showing processes of forming a light-shielding film 14 on the substrate 10 on which lenses 12 have been formed.

[0170] A method of forming a light-shielding film 14 includes at least:

applying the black curable composition of the invention onto the substrate 10 to form a light-shielding coating layer 14A (which may be referred to as the "light-shielding coating layer formation process") (see Fig. 5A);

subjecting the light-shielding coating layer 14A to pattern exposure through a mask 70 (which may be referred to as the "exposure process") (see Fig. 5B); and

developing the light-shielding coating layer 14A after the exposure and then removing an uncured portion, to form a patterned light-shielding film 14 (which may be referred to as the "development process") (see Fig. 5C).

[0171] The light-shielding film 14 may be arbitrarily formed either before or after producing the lens 12. In the following, a method of forming a patterned light-shielding film after the lens 12 has been produced will be described in detail.

Hereinafter, the respective steps of the method of forming a light-shielding film 14 will be described.

[0172] *Light-shielding Coating Layer Formation Process*

In the light-shielding coating layer formation process, as shown in Fig. 5A, the black curable composition is coated onto the substrate 10 and the lenses 12 to form a light-shielding

coating layer 14A having a low light reflection ratio, which is formed from the black curable composition. In this case, the light-shielding coating layer 14A is formed so as to cover all of the surface of the substrate 10, and the lens surfaces 12a and the surface of the peripheral portion 12b of the lenses 12.

[0173] The substrate 10 which may also be used in this process is not particularly limited, and examples thereof include soda glass, non-alkaline glass, PYREX (registered mark) glass, quartz glass, and a transparent resin.

The substrate 10 as mentioned herein refers to a configuration including both the lens 12 and the substrate 10 in an embodiment in which the lens 12 and the substrate 10 are integrally formed.

On the substrate 10, an undercoat layer may be provided, if necessary, for improvement of adhesion with an upper layer, prevention of diffusion of material or planarization (flattening) of the surface of the substrate 10.

[0174] Examples of a method of applying the black curable composition on the substrate 10 and lenses 12 include various coating methods such as slit coating, spray coating, an inkjet method, spin coating, cast coating, roll coating, or a screen printing method.

A film thickness immediately after applying the black curable composition is preferably from 0.1 μm to 10 μm , more preferably from 0.2 μm to 5 μm , and even more preferably from 0.2 μm to 3 μm , from the viewpoints of thickness uniformity of the coating film, and ease of drying of the coating solvent.

[0175] The drying (prebaking) of the light-shielding coating layer 14A coated on the substrate 10 may be performed using a hot plate, an oven, or the like at a temperature of 50°C to 140°C for 10 seconds to 300 seconds.

[0176] The coating film thickness after drying the black curable composition (hereinafter also simply referred to as "dry film thickness") may be arbitrarily selected according to desired performances such as a light-shielding property, and is generally in a range from about 0.1 μm to less than 50 μm .

[0177] *Exposure Process*

In the exposure process, the light-shielding coating layer 14A formed in the light-shielding coating layer formation process is subjected to patternwise exposure. The patternwise exposure may be performed by scanning exposure, but as shown in Fig. 5B, exposure through a mask 70 having a predetermined mask pattern is preferable.

[0178] In the exposure in this process, the coating layer 14A is exposed to light through a mask having a predetermined mask pattern, whereby only a portion irradiated with light is cured in the coating layer 14A. A mask pattern is used through which the surfaces of the

lens peripheral portions 12b and the surface of the substrate 10 present between the lenses 12 are irradiated with light. Therefore, only the light-shielding coating layer 14A present at regions other than the lens surfaces 12a is cured by light irradiation, and the cured regions form a light-shielding film 14.

[0179] As the radiation which may be used for the exposure, ultraviolet rays such as g-rays, h-rays, or i-rays are preferably used. The radiation may be from a light source of a single wavelength or may be from a light source including all wavelengths such as a high-pressure mercury lamp.

[0180] *Development Process*

Subsequently, by performing an alkali development treatment (development process), a portion which has not been irradiated by light during the exposure, that is, an uncured portion of the light-shielding coating layer 14A, is eluted into an aqueous alkali solution, and only the portions cured by light irradiation remain.

Specifically, when the light-shielding coating layer 14A exposed as shown in Fig. 5B is developed, only the light-shielding coating layer 14A that has been formed on the lens surfaces 12a are removed, and a cured light-shielding film 14 is formed in the other regions than the lens surfaces 12a, as shown in Fig. 5C.

[0181] An alkali agent contained in a developer (i.e., an aqueous alkali solution) used in the development process may be any one of an organic alkali agent, an inorganic alkali agent, and a combination of an organic alkali agent and an inorganic alkali agent. It is preferable to use an organic alkali developer in forming the light-shielding film in the invention, from the viewpoints of reduced likelihood of impairing a peripheral circuit.

Examples of the alkali agent used in a developer include organic alkali compounds (i.e., organic alkali agents) such as aqueous ammonia, ethylamine, diethylamine, dimethylethanolamine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, choline, pyrrole, piperidine, or 1,8-diazabicyclo-[5,4,0]-7-undecene; and inorganic compounds (i.e., inorganic alkali agents) such as sodium hydroxide, potassium hydroxide, sodium hydrogen carbonate, or potassium hydrogen carbonate. An aqueous alkali solution obtained by diluting any one of these alkali agents with pure water to a concentration of from 0.001% by mass to 10% by mass, and preferably from 0.01% by mass to 1% by mass, is preferably used as a developer.

[0182] In general, development is carried out at a temperature of 20°C to 30°C for a developing time of 20 seconds to 90 seconds.

[0183] When a developer formed from the aqueous alkali solution is used, generally an unexposed portion of a coating film is removed by the developer, followed by washing

(rinsing) with pure water. In other words, after a development treatment, an excess developer is washed away and removed satisfactorily with pure water, and a drying step is subsequently performed.

[0184] Moreover, the production method may further include, if necessary, a step of curing the formed light-shielding film (i.e., light-shielding pattern) by heating (i.e., post-baking) and/or light exposure, after performing the light-shielding coating layer formation process, the exposure process, and the development process.

[0185] The post-baking is a heating treatment performed after development, for the purpose of complete curing, and is generally a heat curing treatment at 100°C to 250°C. The conditions such as temperature and times of post-baking may be suitably set depending on the materials of the substrate 10 or the lens 12. For example, when the substrate 12 is a glass, the post-baking temperature is preferably from 180°C to 240°C.

The post-baking treatment of a light-shielding film 14 formed through the development may be performed in a continuous system or a batch system using a heating apparatus such as a hot plate, a convection oven (hot-air circulating dryer), or a radio-frequency heating apparatus under the above-mentioned conditions.

[0186] In the above-mentioned procedure, an embodiment in which the lens 12 has a concave shape is described. However, the shape of the lens is not specifically limited thereto, and the lens may have a convex or aspheric surface. Furthermore, in the above-mentioned procedure, an embodiment in which a wafer level lens having plural lenses 12 formed on one side of a substrate 10 is described. However, a wafer level lens of the invention may have a configuration in which plural lenses 12 are formed on both sides of a substrate 10, and in this case, light-shielding layers 14 are formed on both sides of the substrate 10 in regions other than the lens surfaces.

[0187] *Configuration and Production of Wafer Level Lens (2)*

Fig. 6 is a view showing another configuration example of a wafer level lens array.

The wafer level lens array shown in Fig. 6 has a configuration (monolithic type) in which a substrate 10 and lenses 12 are formed at once using the same molding material.

Examples of molding materials used for forming such a wafer level lens array are the same as the molding materials described above. In this embodiment, plural concave lenses 12 are formed on one side (upper side in figure) of the substrate 10, and plural convex lenses 20 are formed on the other side (lower side in figure) of the substrate. A patterned light-shielding film 14 is formed in regions of the substrate 10 excluding the lens surface 12a, at the side on which the plural concave lenses 12 are formed; that is, a patterned light-shielding film 14 is formed on the surface of the substrate 10 and the surface of the lens peripheral portions

12b. As a patterning method used for forming the light-shielding film 14, any of the methods described above may be used.

[0188] *Configuration and Production of Wafer Level Lens (3)*

With reference to Figs. 7A to 7C and Fig. 8A to 8C, another configuration example of a wafer level lens array and the procedures for producing the same will be described below.

Here, Figs. 7A to 7C are schematic views showing another embodiment of processes for forming a patterned light-shielding film 14.

Further, Figs. 8A to 8C are schematic views showing processes for molding lenses 12 after the patterned light-shielding film 14 has been formed.

[0189] In the embodiments of the wafer level lens array shown in Figs. 3 to 6, the patterned light-shielding film 14 is formed on the substrate 10 on which the lenses 12 have been formed. In contrast, in the embodiment described below, a patterned light-shielding film 14 is first formed on a substrate 10, and then lenses 12 are molded on the substrate 10.

[0190] *Formation of Light-shielding Film*

First, as shown in Fig. 7A, a light-shielding coating layer forming process, in which a black curable composition is coated onto the substrate 10 to form a light-shielding coating layer 14A, is carried out.

[0191] Thereafter, the light-shielding coating layer 14A coated on the substrate 10 is dried using a hot plate, an oven, or the like at a temperature of 50°C to 140°C for 10 seconds to 300 seconds. The dry film thickness of the black curable composition may be arbitrarily selected according to desired performances such as a light-shielding property, and is in a range from about 0.1 μm to less than 50 μm .

[0192] Next, as shown in Fig. 7B, the light-shielding coating layer 14A formed in the light-shielding coating layer formation process is subjected to pattern exposure through a mask 70. The mask 70 has a predetermined mask pattern.

In this light exposure step, the light-shielding coating layer 14 is subjected to pattern exposure, whereby only a portion which is irradiated by light is cured in the light-shielding coating layer 14A. In this embodiment, a mask pattern is used which enables light irradiation at a portion of the light-shielding coating layer 14A in a region excluding the regions which serve as lens apertures 14a of lenses 12 when the lenses 12 are molded in the subsequent processes. In this way, the light-shielding coating layer 14A is cured by light-irradiation excluding portions thereof which are to become the lens apertures 14a of the lenses 12. Examples of radiation which may be used in the exposure preferably include ultraviolet rays such as g-rays, h-rays, or i-rays, as in the above-mentioned procedures.

[0193] Next, by performing an alkali development treatment (developing process), only the

light-shielding coating layer 14A in the region corresponding to the lens aperture 14a of the lens 12 which is an uncured region of the light-shielding coating layer 14A in the pattern exposure is eluted by an aqueous alkali solution. At this time, as shown in Fig. 7C, a photocured light-shielding coating layer 14A remains on the substrate 10 except for the regions for the lens apertures 14a of the lenses 12, whereby a light-shielding film 14 is formed.

Here, examples of the alkaline agent in the aqueous alkali solution as a developer are the same as those used in the procedures described above.

Then, after the developing treatment, an excess developer is washed and removed, followed by drying.

[0194] Also in the present embodiment, a step of curing the formed light-shielding film by post-baking and/or light exposure as described above may be carried out, if necessary, after performing the light-shielding coating layer formation process, the exposure process, and the development process.

[0195] *Formation of Lens*

Next, a step of forming the lenses 12, which is performed after the light-shielding film 14 is formed, will be described.

As shown in Fig. 8A, a molding material M for lenses 12 is applied dropwise using a dispenser 50 onto a substrate 10 on which the patterned light-shielding film 14 has been formed. The molding material M for lenses 12 is supplied so as to cover regions corresponding to the lens apertures 14a of the lenses 12 and so as to also cover a portion of the end of the light-shielding film 14 adjacent to the apertures.

[0196] After the molding material M is supplied to the substrate 10, a mold 80 for forming a lens is disposed over the substrate at the side of the substrate 10 where the molding material M has been supplied, as shown in Fig. 8B. The mold 80 has plural concave sections 82 for transferring the shape of lens 12 according to the desirable number of lenses 12.

[0197] Then, the mold 80 is pressed onto the molding material M present on the substrate 10, so that the molding material M is deformed according to the shape of the concave sections. The molding material M is cured while the mold 80 is pressed onto the molding material M, by irradiation of heat or ultraviolet light from the outside of the mold when the molding material M is a thermosetting resin or an ultraviolet curable resin.

[0198] After the molding material M is cured, the substrate 10 and the lenses 12 are released from the mold 80, thereby obtaining a wafer level lens array including a patterned light-shielding film 14 on the substrate 10, as shown in Fig. 8C.

[0199] As described above, the patterned light-shielding film 14 included in a wafer level lens is formed not only in a region excluding the lens surfaces 12a of the lenses 12 as shown

in Fig. 5, but the light-shielding film 14 may also be provided in a region excluding the lens apertures 14a of the lenses 12 as shown in Fig. 8C.

[0200] Since the wafer level lens has a light-shielding film 14 which has a low light reflection ratio and is patternwise formed on at least one side of the substrate 10, generation of reflected light is inhibited while light is sufficiently shielded in a region other than at the lens surfaces 12a or the lens apertures 14a of the lenses 12. Therefore, when the wafer level lens is applied to an imaging module having a solid imaging device, defects such as ghosting or flare caused by reflected light during imaging are prevented.

[0201] Furthermore, since the light-shielding film 14 is provided on the surface of the substrate, other light-shielding members need not be placed in the wafer level lens, and an increase in production cost is suppressed.

[0202] As in the configuration described in International Application Publication No. WO 2008/102648 mentioned above, when the surface around the lens has a concave and convex structure, incident light on the structure is reflected or diffused, and thus there is a risk of causing defects such as ghosting. In this regard, as shown in Fig. 5, when the patterned light-shielding film 14 is provided in a region excluding the lens surface 12a of the lens 12, light is shielded in other regions than at the lens surface 12a and the optical performance is improved.

EXAMPLES

[0203] Hereinbelow, the invention is described in detail with reference to Examples, but is not limited to the following Examples unless departing from the spirit of the invention.

Further, unless otherwise specified, "%" and "part(s)" are on the basis of mass.

[0204] *Preparation of Titanium Black Dispersion (TB-1 Dispersion)*

The components shown in Composition I below were subjected to a high viscosity dispersion treatment using a twin roll, thereby obtaining a dispersion. The viscosity of this dispersion was 40,000 mPa·s.

Further, the components may be kneaded using a kneader for 30 minutes before the high viscosity dispersion treatment.

[0205] (Composition I)

· Titanium black 13 M-C having an average primary particle diameter of 75 nm
(manufactured by Mitsubishi Materials Electronic Chemicals Co., Ltd.) (Pigment Black 35)
40 parts

· Propylene glycol monomethyl ether acetate solution of benzyl methacrylate
(BzMA)/methacrylic acid (MAA) copolymer (BzMA/MAA = 60/40 (molar ratio), Mw:

30,000, solid content: 40% by mass)

8 parts

· SOLSPERSE 5000 (manufactured by The Lubrizol Corporation)

2 parts

[0206] The components shown in Composition II below were added to the thus-obtained dispersion, followed by stirring using a homogenizer for 3 hours under the conditions of 3,000 rpm. The thus-obtained mixed solution was subjected to a fine dispersion treatment using a disperser (trade name: DISPERMAT, manufactured by Getzmann) employing zirconia beads having a diameter of 0.3 mm for 4 hours, thereby obtaining a titanium black dispersion (hereinafter denoted as a TB-1 dispersion).

The viscosity of the TB-1 dispersion was 6.8 mPa·s.

[0207] (Composition II)

· Propylene glycol monomethyl ether acetate solution of benzyl methacrylate

(BzMA)/methacrylic acid (MAA) copolymer (BzMA/MAA = 70/30 (molar ratio), Mw: 30,000, solid content 40% by mass)

10 parts

· Propylene glycol monomethyl ether acetate

200 parts

[0208] *Preparation of Titanium Black Dispersion (TB-2 Dispersion)*

The components shown in Composition III below were subjected to a high viscosity dispersion treatment using a twin roll, thereby obtaining a dispersion. The viscosity of this dispersion was 40,000 mPa·s.

Further, the components may be kneaded using a kneader for 30 minutes before the high viscosity dispersion treatment.

[0209] (Composition III)

· Titanium black having an average primary particle diameter of 40 nm (manufactured by Mitsubishi Materials Electronic Chemicals Co., Ltd.)

40 parts

· Exemplary Compound 72

5 parts

[0210] The components shown in Composition IV below were added to the thus-obtained dispersion, followed by stirring using a homogenizer for 3 hours under the conditions of 3,000 rpm. The thus-obtained mixed solution was subjected to a fine dispersion treatment using a disperser (trade name: DISPERMAT, manufactured by Getzmann) employing zirconia beads having a diameter of 0.3 mm for 4 hours, thereby obtaining a titanium black dispersion (hereinafter denoted as a TB-2 dispersion).

The viscosity of the TB-2 dispersion was 6.8 mPa·s.

[0211] (Composition IV)

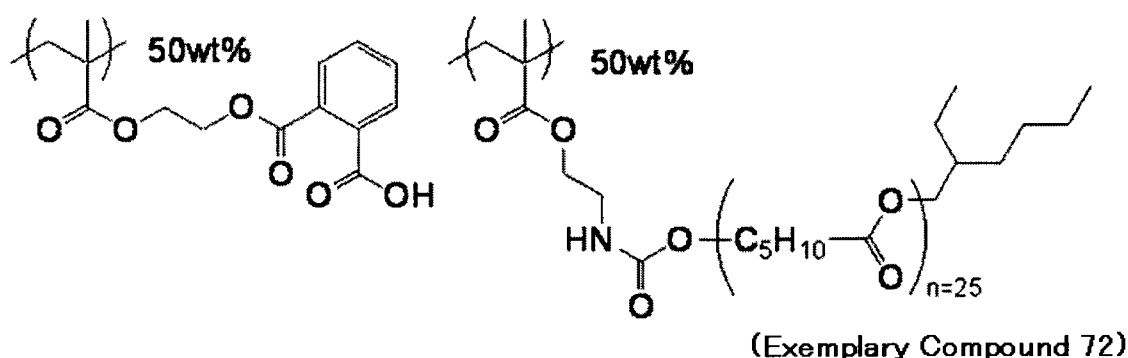
· Exemplary Compound 72

5 parts

· Propylene glycol monomethyl ether acetate

200 parts

[0212]

[0213] *Method for Synthesizing Exemplary Compound 72*

Exemplary Compound 72 may be synthesized in accordance with the preparation method described in paragraphs [0338] to [0340] of JP-A No. 2010-106268.

[0214] *Preparation of Carbon Black Dispersion (CB Dispersion)*

A carbon black dispersion (CB dispersion) was obtained by replacing the titanium black of TB-1 dispersion with the same mass of carbon black (carbon black MA-100 R (manufactured by Mitsubishi Chemical Corporation)).

[0215] *Preparation of Silver Tin dispersion (ST dispersion)*

A solution obtained by dissolving 15 g of tin colloid (average particle diameter: 20 nm, solid content: 20%, manufactured by Sumitomo Osaka Cement Co., Ltd.), 60 g of silver colloid (average particle diameter: 7 nm, solid content: 20% by weight, manufactured by Sumitomo Osaka Cement Co., Ltd.), and 0.75 g of polyvinyl pyrrolidone in 100 mL of water was added to 200 mL of pure water with a temperature maintained at 60°C, thereby obtaining a colloidal solution.

Subsequently, the colloidal solution was stirred for 60 minutes with the temperature maintained at 60°C, followed by application of ultrasonic waves for 5 minutes. Subsequently, the colloidal solution was concentrated by centrifugation to obtain a mixed solution having a 25% solid content. The mixed liquid then was dried by a freeze-drying method, thereby obtaining a powder sample.

A silver tin dispersion (ST dispersion) was obtained by replacing the titanium black in the TB-1 dispersion with the same mass of the thus-obtained powder sample.

[0216] *Examples 1 to 5, and Comparative Examples 1 and 2*

1. Preparation of Black Polymerizable Composition

The components of the following composition A-1 were mixed using a stirrer to prepare each of the black polymerizable compositions used in Examples 1 to 5 and

Comparative Examples 1 and 2.

(Composition A-1)

· (D) Alkali-soluble binder polymer mentioned in Table 1	2.5 parts
· (C) Polymerizable compound: dipentaerythritol hexaacrylate	2.0 parts
· (C) Polymerizable compound: pentaerythritol triacrylate	1.0 part
· (B) Polymerization initiator mentioned in Table 1	0.3 parts
· Dispersion containing (A) black pigment, mentioned in Table 1	24 parts
· Propylene glycol monomethyl ether acetate	10 parts
· Cyclohexanone	8 parts

[0217] 2. Production and Evaluation of Light-Shielding Film (Light-Shielding Region)

Each black polymerizable composition obtained above was applied on a glass wafer by spin coating, and heated on a hot plate at a temperature of 120°C for 2 minutes, thereby obtaining a black polymerizable composition coating layer.

Subsequently, the thus-obtained coating layer was exposed to light at an amount of 500 mJ/cm² using an i-ray stepper.

The coating layer after the exposure was repeatedly subjected to paddle development five times using a 0.3% aqueous tetramethylammonium hydroxide solution at a temperature of 23°C for 60 seconds. Subsequently, the coating layer was rinsed using a spin shower, and further washed with pure water, thereby obtaining a patterned light-shielding film.

For the thus-obtained light-shielding film pattern, the number of repeated development when the peeling of an exposed portion was found was determined using an optical microscope, and results thereof are shown in Table 1.

When the number of repeated development is 4 or more, it is estimated that alkali developer resistance is good.

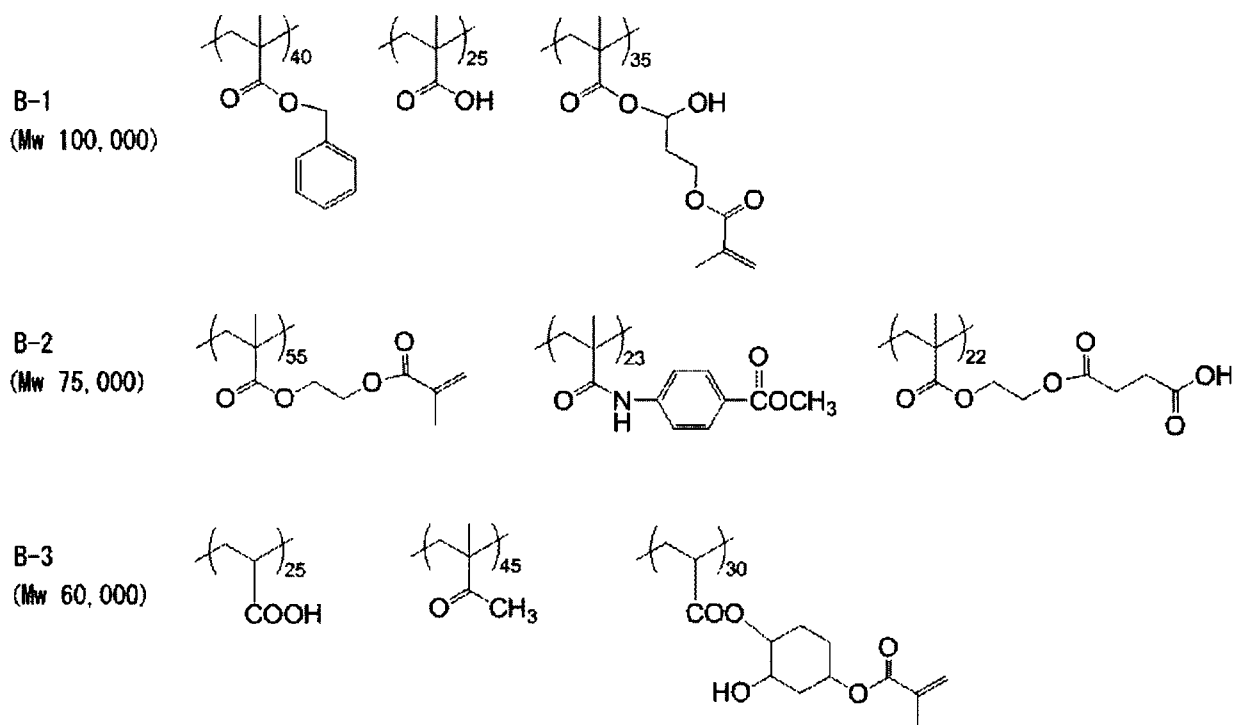
[0218] Table 1

	Dispersion	(D) Alkali-soluble binder	(B) Polymerization initiator	Number of development
Example 1	TB-1	B-1	I-1	5
Example 2	TB-2	B-2	I-1	5 or more
Example 3	TB-2	B-2	I-2	5 or more
Example 4	CB	B-3	I-1	4
Example 5	ST	B-3	I-3	4
Comparative Example 1	CB	HB-1	I-1	2
Comparative Example 2	CB	HB-3	I-1	2

[0219] The structures of compounds B-1 to B-3 and HB-1 to HB-3 mentioned in Tables 1 and 2 are shown below. The numeral values of the compositional ratios in the following structures indicate the contents (% by mass (wt%)) of the structural units.

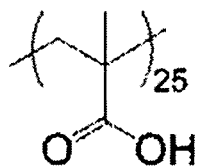
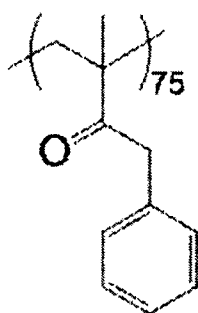
The structures of polymerization initiators I-1 to I-3 are also shown.

[0220]

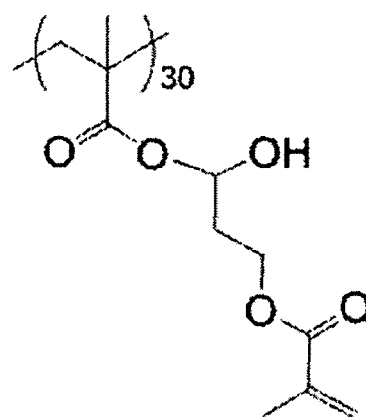
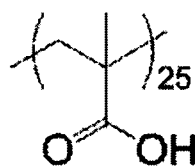
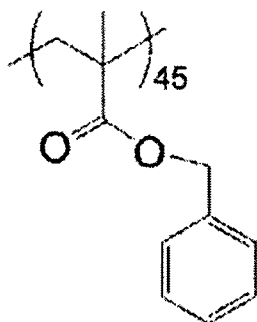


[0221]

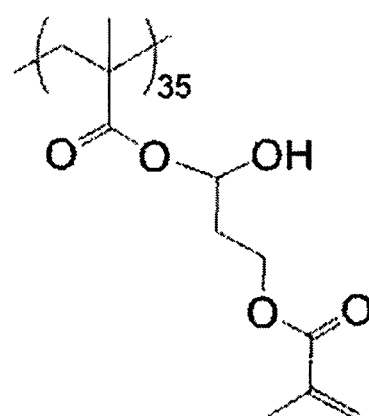
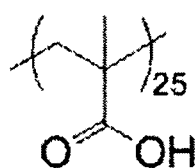
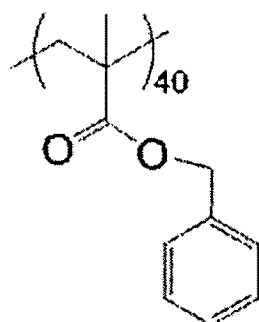
HB-1
(Mw 60,000)



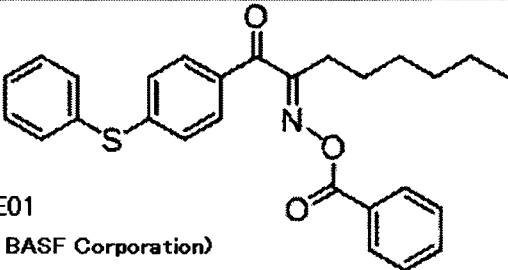
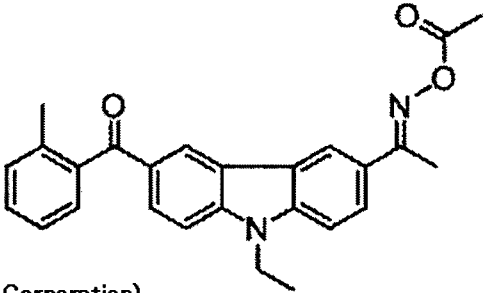
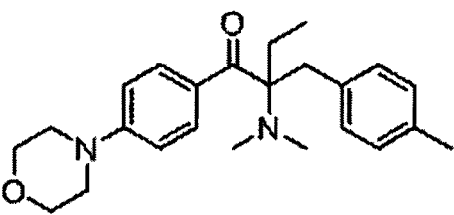
HB-2
(Mw 15,000)



HB-3
(Mw 28,000)



[0222]

Polymerization initiator	
Compound No.	Structure
Compound I-1	 IRGACURE OXE01 (manufactured by BASF Corporation)
Compound I-2	 IRGACURE OXE02 (manufactured by BASF Corporation)
Compound I-3	 IRGACURE 379 (manufactured by BASF Corporation)

[0223] As shown by the results of Table 1, a wafer level lens having a light-shielding film formed from the black polymerizable composition of the invention has an excellent alkali developer resistance.

[0224] *Examples 6 to 10 and Comparative Example 3*

1. Preparation of Black Polymerizable Composition

The components of Composition A-2 described below were mixed using a stirrer, thereby obtaining the black polymerizable compositions of Examples 6 to 10 and Comparative Example 3, respectively.

(Composition A-2)

- (D) Alkali-soluble binder polymer mentioned in Table 2 2.5 parts
- (C) Polymerizable compound: succinic acid-modified monomer of dipentaerythritol hexaacrylate 2.0 parts
- (C) Polymerizable compound: pentaerythritol triacrylate 2.0 part

· 3-Methacryloxypropyl dimethoxymethylsilane	0.1 parts
· (B) Polymerization initiator mentioned in Table 2	0.4 parts
· Dispersion containing (A) black pigment, mentioned in Table 1	24 parts
· Propylene glycol monomethyl ether acetate	10 parts
· Cyclohexanone	8 parts

[0225] 2. Production and Evaluation of Light-Shielding Film (Light-Shielding Region)

The following composition V was coated on a glass wafer to a film thickness of 15 μm , and subjected to patternwise exposure using a 50- μm hole mask to give a cylindrical diameter of 50 μm , by a high pressure mercury lamp, thereby forming a transparent resin layer having a cylindrical hole having a diameter of 50 μm . Subsequently, the transparent resin layer was heated on a hot plate at a temperature of 200°C for 5 minutes, thereby obtaining a wafer including a transparent resin layer on which holes were formed.

Subsequently, each of the black polymerizable compositions obtained above was spray-coated using a two-fluid type spray-coating apparatus on the wafer having a transparent resin layer formed thereon, and dried at 120°C for 2 minutes, thereby obtaining a black polymerizable composition layer having an average film thickness of 3 μm . It was found that the black polymerizable composition layer thus formed was uniformly formed on the surface of the glass wafer and the surface of the transparent resin layer, even with the structures having unevenness.

Moreover, a hole-forming region of the transparent resin layer and a hole portion of the photomask were in conjunction with each other for performing positioning, and light exposure was carried out using a photomask having a light-shielded hole portion having a diameter of 50 μm , at an exposure amount of 1,000 mJ/cm^2 using a high pressure mercury lamp or the like, from the top of the black polymerizable composition layer. By exposure, the black polymerizable composition layer is cured in the region other than the hole-forming region formation, and the black polymerizable composition layer of the hole-forming region is present in an uncured state due to the hole mask.

(Composition V)

· Allyl methacrylate/methacrylic acid copolymer (molar ratio 70/30; Mw=50,000)	1.6 parts
· Dipentaerythritol hexaacrylate ((C) polymerizable compound)	2.0 parts
· Pentaerythritol triacrylate ((C) polymerizable compound)	1.0 part
· IRGACURE OXE-01 (manufactured by BASF)	0.3 parts
· Propylene glycol monomethyl ether acetate	5 parts

[0226] The coating layer after the light exposure was repeatedly subjected to paddle development using a 0.3% aqueous tetramethylammonium hydroxide solution at a temperature of 23°C for 60 seconds. Subsequently, the coating layer was rinsed using a spin shower, and further washed with pure water, thereby obtaining a patterned light-shielding film.

The number of developments at which peeling was observed is shown in Table 2. It is estimated that a higher number of development indicates a better alkali developer resistance.

In addition, the residue of the cylindrical transparent resin layer portion was developed twice, and a case in which no residue was found is denoted as "A", and a case in which residues were found is denoted as "B", respectively, in Table 2.

The results are shown in Table 2.

[0227] Table 2

	Dispersion	(D) Alkali- soluble binder	(B) Polymerization initiator	Residue	Number of developments
Example 6	TB-1	B-1	I-1	A	5
Example 7	TB-2	B-2	I-2	A	6 or more
Example 8	TB-2	B-2	I-3	A	6 or more
Example 9	CB	B-3	I-2	A	4
Example 10	ST	B-3	I-1	A	3
Comparative Example 3	CB	HB-2	I-1	B	2

[0228] As apparent from the results of Table 2 above, in a wafer level lens having a light-shielding film formed from the black polymerizable composition of the invention, the amount of residues in a non-image portion was reduced, and peeling of the image portion was suppressed, which means an excellent alkali developer resistance. Further, it was found that the black polymerizable composition of the invention is capable of being spray-coated.

[0229] From the results described above, it was found that the black polymerizable composition of the invention has an excellent alkali developer resistance. It was also found that a black polymerizable composition capable of being spray-coated is provided.

[0230] Japanese Patent Application Nos. 2010-225100 and 2011-003422 is 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.

1. A black polymerizable composition, comprising:
 - (A) a black material;
 - (B) a polymerization initiator;
 - (C) a polymerizable compound; and
 - (D) an alkali-soluble binder polymer having a weight average molecular weight of at least 30,000 and having a polymerizable group at a side chain thereof.
2. The black polymerizable composition according to claim 1, wherein the (A) black material comprises titanium black.
3. The black polymerizable composition according to claim 1 or 2, wherein the (D) alkali-soluble binder polymer comprises an alkali-soluble binder polymer having a weight average molecular weight of from 50,000 to 100,000 and having a polymerizable group at a side chain thereof.
4. The black polymerizable composition according to any one of claims 1 to 3, which is used for forming a light-shielding region of a wafer level lens.
5. The black polymerizable composition according to any one of claims 1 to 4, which is capable of being spray-coated.
6. The black polymerizable composition according to any one of claims 1 to 5, wherein the total solid content in the black polymerizable composition is from 20% by mass to 35% by mass.
7. The black polymerizable composition according to any one of claims 1 to 6, wherein the polymerizable group included in the (D) alkali-soluble binder polymer comprises an acryl group, a methacryl group, a styryl group, an allyl group, an acrylamide group, a methacrylamide group, a vinyl group or a vinyl ether group.
8. The black polymerizable composition according to any one of claims 1 to 7, wherein a content of the (D) alkali-soluble binder polymer is from 5% by mass to 75% by mass with respect to the total solid content of the black polymerizable composition.

9. A method for producing a black layer, the method comprising:
applying, by spray coating, the black polymerizable composition according to any one of claims 1 to 8 onto a surface of a solid to form a black polymerizable composition layer;
and
applying energy to the formed black polymerizable composition layer to cure the formed black polymerizable composition layer.
10. The method for producing a black layer according to claim 9, wherein the surface of the solid is a surface of a peripheral portion of a wafer level lens, and the black layer is a light-shielding region formed in the peripheral portion of a wafer level lens.