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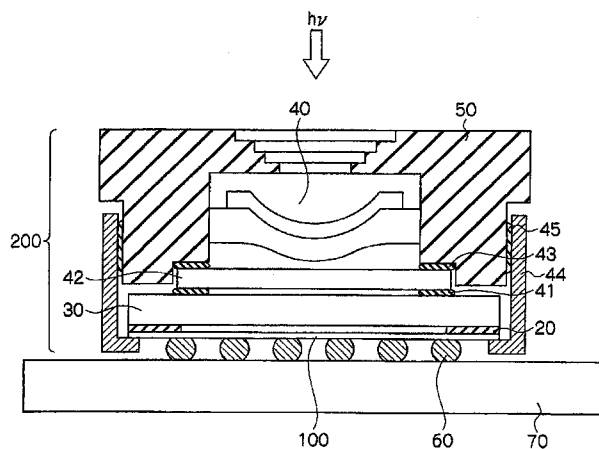
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FIG. 1



(57) Abstract: There is provided a polymerizable composition exhibiting high light-blocking effect in the infrared region and high light transparency in the visible region and being capable of forming a pattern with excellent resolution by alkali development, and a photosensitive layer, a permanent pattern, a wafer-level lens, a solid-state imaging device and a pattern forming method, each using the composition; and the composition contains a polymerization initiator, a polymerizable compound, a tungsten compound, an alkali-soluble binder, and an inorganic filler.

DESCRIPTION

Title of Invention

POLYMERIZABLE COMPOSITION, AND PHOTSENSITIVE LAYER, PERMANENT PATTERN, WAFER-LEVEL LENS, SOLID-STATE IMAGING DEVICE AND PATTERN FORMING METHOD, EACH USING THE COMPOSITION

Technical Field

The present invention relates to a polymerizable composition, particularly, a polymerizable composition suitably usable for the formation of a solder resist, and a photosensitive layer, a permanent pattern, a wafer-level lens, a solid-state imaging device and a pattern forming method, each using the composition.

Background Art

A solid-state imaging device (image sensor) used in cellular phones, digital cameras, digital videos, monitoring cameras and the like is a photoelectric conversion device having an integrated circuit formed using the production technique of a semiconductor device. In recent years, with reduction in size and weight of a cellular phone or a digital camera, the solid-state imaging device is required to be more downsized.

For downsizing the solid-state imaging device, a technique of applying a through-electrode or thinning a silicon wafer has been proposed (see, for example, JP-A-2009-194396 (the term "JP-A" as used herein means an "unexamined published Japanese patent application")). Downsizing can be realized by polishing and thereby thinning the silicon wafer, but due to thinning of the silicon wafer, light at a wavelength of 800 nm or more is liable to be transmitted, though the effect of blocking light at 800 nm or less is maintained. A photodiode used in the solid-state imaging device reacts also to light at a wavelength of 800 to 1,200 nm, and transparency to light at a wavelength of 800 nm or more is found to cause a new problem that the pictorial quality is deteriorated.

The solid-state imaging device has a configuration that a color filter and a lens are provided adjacently to one side of a photodiode, an infrared cut filter is present in the vicinity of the color filter or lens to cut light at a wavelength of 800 to 1,200 nm, and a metal wiring, a

solder resist and the like are present on the opposite side of the color filter. For example, the space between metal wirings is filled with a solder resist in many cases, but there is a problem that infrared light such as leakage light intruding into the inside of a cellular phone, a digital camera or the like cannot be cut by the solder resist. To cope with this problem, a technique of further providing an infrared-blocking layer on the outer side of the solder resist poor in the light-blocking effect for infrared light and thereby ensuring the infrared-blocking effect has been conventionally employed. However, a height difference due to wiring or the like is generally present on the solder resist and an infrared-blocking layer material can be hardly coated to a uniform thickness on a substrate surface having a height difference, which gives rise to a problem that if a thin portion exists, light is transmitted therethrough.

In order to provide an infrared-blocking layer only in a desired portion, the composition preferably exhibits photosensitivity and has a photolithography performance enabling patterning by exposure. The light-blocking photosensitive composition having a photolithography performance includes a black resist using carbon black employed for the formation of an LCD color filter. The carbon black has a high light-blocking effect in the visible region but exhibits a low light-blocking effect in the infrared region and when it is attempted to apply such a black resist as a solder resist, if carbon black is added in an amount large enough to ensure the required light-blocking effect in the infrared region, this causes a problem that the light-blocking effect in the visible region becomes excessively high, light at a shorter wavelength than the visible region, which is usually employed for image formation and used at the exposure to high-pressure mercury lamp, KrF, ArF or the like, is also cut to incur reduction in the sensitivity, making it impossible to obtain sufficient photo-curability, and an excellent pattern cannot be obtained even through a development step using an alkali developer.

Also, at present, an infrared-blocking layer is separately provided after forming a solder resist by a coating method and therefore, in the solder resist formation and the infrared-blocking layer formation, steps such as coating, exposure, development and post-heating must be performed a plurality of times, which leads to a cumbersome process and a rise in the cost. In this regard, improvements are required.

For meeting the requirement, it has been attempted to impart a light-blocking effect to the solder resist itself, and, for example, a black solder resist composition containing a black colorant, a colorant other than black, and a polyfunctional epoxy compound has been proposed (see, for example, JP-A-2008-257045). However, this composition is characterized in that

the content of the black colorant is kept low by using a colorant other than black in combination, and is practically insufficient from the standpoint of satisfying both light-blocking effect, particularly light-blocking effect in the infrared region, and pattern formability.

Summary of Invention

Moreover, for the purpose of detecting the position of a semiconductor substrate by a visible light sensor in the process of producing a solid-state imaging device, an alignment mark in a protruded form is often provided at the predetermined position on the surface on the metal wiring and solder resist side (that is, the surface opposite the color filter or lens) of a semiconductor substrate of a solid-state imaging device.

In the case of the above-described configuration where an infrared-blocking layer is further provided on the outer side of the solder resist lacking the light-blocking effect for infrared light, it is considered that even when the infrared-blocking layer is a layer having a light-blocking effect also for visible light, the thickness of this layer need not be so large for the infrared-blocking purpose (because the infrared-blocking purpose can be achieved by a thinner film than the solder resist layer) and therefore, the detection by a visible light sensor does not face a serious trouble due to covering of the alignment mark with the infrared-blocking layer. However, particularly in the configuration where, as in JP-A-2008-257045, a black colorant is contained in the solder resist composition for imparting a light-blocking effect to the solder resist itself, when the alignment mark is covered with a solder resist layer, maybe due to the thickness of the solder resist layer, a trouble that the alignment mark is not detected by the visible light sensor is liable to more often occur.

Under these circumstances, a polymerizable composition ensuring high light-blocking effect in the infrared region and high light transparency in the visible region and being capable of forming an excellent pattern by alkali development is demanded at present.

Incidentally, JP-A-2009-205029 discloses a technique of using an inorganic near infrared absorber-containing layer as a near infrared-absorbing layer for an image display device, and, for example, a coating solution for near infrared-absorbing layer formation, containing a polymerizable compound, a polymerization initiator and a near infrared absorber, is described in its working examples.

Also, JP-A-2006-201463 discloses a technique of using a near infrared absorber-containing layer as a high refractive index layer in an antireflection film, and, for example, a coating solution for hardcoat formation, containing an active energy ray-curable compound, a

polymerization initiator and a near infrared absorber, is described in its working examples.

However, the layer obtained from these coating solutions is not subjected to pattern formation through exposure and alkali development. Actually, this layer is, even in the unexposed region, insufficient in solubility for an alkali developer and has substantially no alkali developability.

The present invention has been made by taking into consideration these current circumstances, and the task of the present invention is to solve those conventional various problems and attain the following object.

That is, an object of the present invention is to provide a polymerizable composition exhibiting high light-blocking effect in the infrared region and high light transparency in the visible region and being capable of forming a pattern with excellent resolution by alkali development, and a photosensitive layer, a permanent pattern, a wafer-level lens, a solid-state imaging device and a pattern forming method, each using the composition.

Another object of the present invention is to provide a polymerizable composition ensuring that when the substrate on which a photosensitive layer is provided has an uneven shape, a photosensitive layer having a shape successfully following the uneven shape of the substrate can be formed, and a photosensitive layer, a permanent pattern, a wafer-level lens, a solid-state imaging device and a pattern forming method, each using the composition.

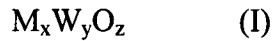
The present invention has the following configurations, and the above-described objects can be attained by these configurations.

- (1) A polymerizable composition comprising:
a polymerization initiator,
a polymerizable compound,
a tungsten compound,
an alkali-soluble binder, and
an inorganic filler.
- (2) The polymerizable composition as described in (1) above, wherein the inorganic filler is silica.
- (3) The polymerizable composition as described in (1) or (2) above, wherein the alkali-soluble binder has an acid group.
- (4) The polymerizable composition as described in any one of (1) to (3) above, wherein the acid group is a phenolic hydroxyl group or a thiol group.
- (5) The polymerizable composition as described in any one of (1) to (4) above, wherein

the alkali-soluble binder has a crosslinking group.

(6) The polymerizable composition as described in any one of (1) to (5) above, wherein the polymerization initiator is an acetophenone-based compound and the polymerizable composition further contains a sensitizer.

(7) The polymerizable composition as described in any one of (1) to (6) above, wherein the tungsten compound is represented by the following formula (I):



wherein M represents a metal, W represents tungsten, O represents oxygen,

$0.001 \leq x/y \leq 1.1$, and

$2.2 \leq z/y \leq 3.0$.

(8) The polymerizable composition as described in (7) above, wherein M is an alkali metal.

(9) The polymerizable composition as described in any one of (1) to (8) above, wherein the polymerizable compound is a polyfunctional polymerizable compound having a plurality of polymerizable groups within the molecule.

(10) The polymerizable composition as described in any one of (1) to (9) above, which is used for a solder resist.

(11) A photosensitive layer formed of the polymerizable composition described in any one of (1) to (10) above.

(12) A permanent pattern formed of the polymerizable composition described in any one of (1) to (10) above.

(13) The permanent pattern as described in (12) above, wherein the permanent pattern is a solder resist layer.

(14) The permanent pattern as described in (12) above, wherein the permanent pattern is an infrared-blocking film.

(15) A wafer-level lens having a lens and the permanent pattern described in (12) above formed in the circumferential edge part of the lens.

(16) A solid-state imaging device having the permanent pattern described in any one of (12) to (15) above.

(17) A solid-state imaging device comprising:

a solid-state imaging device substrate having formed on one surface thereof an imaging element part, and

an infrared-blocking film provided on the other surface side of the solid-state imaging device substrate,

wherein the infrared-blocking film is the permanent pattern described in (12) above.

(18) A pattern forming method comprising, in order, a step of forming the photosensitive layer described in (11) above, a step of patternwise exposing said photosensitive layer to cure the exposed area, and a step of removing the unexposed area by alkali development to form a permanent pattern.

According to the present invention, a polymerizable composition exhibiting high light-blocking effect in the infrared region and high light transparency in the visible region and being capable of forming a pattern with excellent resolution by alkali development, and a photosensitive layer, a permanent pattern, a wafer-level lens, a solid-state imaging device and a pattern forming method, each using the composition, can be provided.

Furthermore, according to the present invention, a polymerizable composition ensuring that when the substrate on which a photosensitive layer is provided has an uneven shape, a photosensitive layer having a shape successfully following the uneven shape of the substrate can be formed, and a photosensitive layer, a permanent pattern, a wafer-level lens, a solid-state imaging device and a pattern forming method, each using the composition, can be provided.

Brief Description of Drawings

Fig. 1 is a schematic cross-sectional view showing the configuration of a camera module equipped with the solid-state imaging device according to an embodiment of the present invention.

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

Fig. 3 is a plan view showing one example of the wafer-level lens array.

Fig. 4 is a cross-sectional view along line A-A in Fig. 3.

Fig. 5 is a view showing how a molding material working out to a lens is supplied to a substrate.

Figs. 6A to 6C are views showing the procedure of molding a lens on a substrate by using a mold.

Figs. 7A to 7C are schematic views showing the process of forming a patterned

light-blocking film on a substrate having molded thereon a lens.

Fig. 8 is a cross-sectional view showing one example of the wafer-level lens array.

Figs. 9A to 9C are schematic views showing another embodiment of the process of forming a light-blocking film.

Figs. 10A to 10C are schematic views showing the process of molding a lens on a substrate having thereon a patterned light-blocking film.

Fig. 11 is a schematic cross-sectional view showing the state where a photosensitive layer is provided on a substrate having an uneven shape.

Description of Embodiments

The polymerizable composition of the present invention is described in detail below.

In the description of the present invention, when a group (atomic group) is denoted without specifying whether substituted or unsubstituted, the group includes both a group having no substituent and a group having a substituent. For example, "an alkyl group" includes not only an alkyl group having no substituent (unsubstituted alkyl group) but also an alkyl group having a substituent (substituted alkyl group). Also, in the description of the present invention, the viscosity value indicates the value at 25°C.

The polymerizable composition of the present invention contains a polymerization initiator, a polymerizable compound, a tungsten compound, an alkali-soluble binder and an inorganic filler and, if desired, may contain an infrared-blocking material other than the tungsten compound above, a dispersant, a sensitizer, a crosslinking agent, a curing accelerator, an elastomer, a surfactant and other components.

The polymerizable composition of the present invention is, for example, a negative composition and is typically a negative resist composition. The configuration of this composition is described below.

The constituent requirements may be described below based on representative embodiments of the present invention, but the present invention is not limited to these embodiments. Incidentally, in the description of the present invention, the range expressed by "(numerical value) to (numerical value)" means a range including the numerical values before and after "to" as the lower limit and the upper limit, respectively.

In the description of the present invention, the term "(meth)acrylate" indicates acrylate and methacrylate, the term "(meth)acryl" indicates acryl and methacryl, and the term "(meth)acryloyl" indicates acryloyl and methacryloyl. Also, in the description of the present

invention, the "monomeric substance" has the same meaning as "monomer". The "monomer" as used in the present invention is differentiated from an oligomer and a polymer and indicates a compound having a mass average molecular weight of 2,000 or less. In the description of the present invention, the term "polymerizable compound" indicates a compound having a polymerizable group and may be either a monomer or a polymer. The term "polymerizable group" indicates a group participating in the polymerization reaction.

[1] Polymerization Initiator

The polymerization initiator for use in the polymerizable composition of the present invention is not particularly limited but is preferably a photopolymerizable compound. In the case of initiating the polymerization by light, a compound having photosensitivity to light from ultraviolet region to visible region is preferred. Above all, an acetophenone-based compound is most preferred and in this case, it is preferred to use the compound in combination with the later-described sensitizer.

Examples of the polymerization initiator suitable for the present invention are described below, but the present invention is not limited thereto.

Specific examples of the acetophenone-based compound include 2,2-diethoxyacetophenone, p-dimethylaminoacetophenone, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, p-dimethylaminoacetophenone, 4'-isopropyl-2-hydroxy-2-methyl-propiophenone, 1-hydroxy-cyclohexyl-phenyl-ketone, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, 2-tolyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one, 2-methyl-1-(4-methylthiophenyl)-2-morpholinopropan-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, 2-(dimethylamino)-2-[(4-methylphenyl)methyl]-1-[4-(4-morpholinyl)phenyl]-1-butanone, and 2-methyl-1-(4-methylthiophenyl)-2-morpholinopropan-1-one.

Among these, an α -aminoacetophenone-based compound is preferred, and 2-methyl-1-(4-methylthiophenyl)-2-morpholinopropan-1-one is more preferred.

Commercial products of the α -aminoacetophenone-based compound include, for example, IRGACURE 907, IRGACURE 369 and IRGACURE 379 (trade names, all produced by BASF Japan).

One kind of a polymerization initiator may be used alone, or two or more kinds of polymerization initiators may be used in combination.

The content of the polymerization initiator is preferably from 0.01 to 30 mass%,

more preferably from 0.1 to 20 mass%, still more preferably from 0.1 to 15 mass%, based on the entire solid content by mass of the polymerizable composition of the present invention.

[2] Polymerizable compound

The polymerizable composition of the present invention contains a polymerizable compound. The polymerizable compound used here may be any compound as long as it is a compound having, in the molecule, a functional group capable of undergoing a reaction by the effect of at least one of an acid, a radical and heat (in the description of the present invention, such a functional group is sometimes referred to as a "polymerizable group"), and a polyfunctional polymerizable compound having a plurality of polymerizable groups in the molecule is preferred.

Example of the polymerizable compound having a polymerizable functional group capable of reacting to at least one of an acid, a radical and heat, which can be preferably used in the present invention, include an ethylenically unsaturated group-containing compound having an ethylenically unsaturated group such as unsaturated ester functional group, unsaturated amide group, vinyl ether group and allyl group; a methylol compound; a bismaleimide compound; a benzocyclobutene compound, a bisallylnadiimide compound; and a benzoxazine compound.

The polymerizable compound that can be preferably used in the present invention includes a general radical polymerizable compound, and compounds widely known as the compound having an ethylenically unsaturated double bond in this industrial field can be used without any particular limitation.

These compounds have a chemical form of, for example, a monomer, a prepolymer (that is, dimer, trimer or oligomer), or a mixture or copolymer thereof.

Examples of the monomer and a copolymer thereof include an unsaturated carboxylic acid (such as acrylic acid, methacrylic acid, itaconic acid, crotonic acid, isocrotonic acid and maleic acid), its esters and amides, and a copolymer thereof. Preferably, an unsaturated carboxylic acid ester, an ester of an unsaturated carboxylic acid and an aliphatic polyhydric alcohol compound, and amides of an unsaturated carboxylic acid and an aliphatic polyvalent amino compound, are used.

Particularly, an ester of an unsaturated carboxylic acid and an aliphatic polyhydric alcohol compound can develop high hydrophobicity in the exposed area and is preferred because a pattern having a desired profile can be easily formed by alkali development and also,

a pattern having high durability is obtained (in particular, when higher durability is required of the solder resist, for example, when the wiring density of the metal wiring covered with a solder resist is high, the above-described effects are prominent).

In addition, for example, an addition reaction product of unsaturated carboxylic acid esters or amides having a nucleophilic substituent such as hydroxyl group, amino group and mercapto group to monofunctional or polyfunctional isocyanates or epoxies, and a dehydration condensation reaction product with a monofunctional or polyfunctional carboxylic acid, are also suitably used.

An addition reaction product of unsaturated carboxylic acid esters or amides having an electrophilic substituent such as isocyanate group and epoxy group to monofunctional or polyfunctional alcohols, amines or thiols, and a substitution reaction product of unsaturated carboxylic acid esters or amides having a leaving substituent such as halogen group and tosyloxy group with monofunctional or polyfunctional alcohols, amines or thiols, are also preferred. As another example, compounds where the above-described unsaturated carboxylic acid is replaced by an unsaturated phosphonic acid, a styrene or a vinyl ether, may be also used.

The unsaturated carboxylic acid ester is preferably a methacrylic acid ester, and examples thereof include tetramethylene glycol dimethacrylate, triethylene glycol dimethacrylate, neopentyl glycol dimethacrylate, trimethylolpropane trimethacrylate, trimethylolethane trimethacrylate, ethylene glycol dimethacrylate, 1,3-butanediol dimethacrylate, hexanediol dimethacrylate, pentaerythritol dimethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, dipentaerythritol dimethacrylate, dipentaerythritol hexamethacrylate, sorbitol trimethacrylate, sorbitol tetramethacrylate, bis[p-(3-methacryloxy-2-hydroxypropoxy)phenyl]dimethylmethane, bis-[p-(methacryloxyethoxy)phenyl]dimethylmethane, and their EO-modified or PO-modified products.

The unsaturated carboxylic acid ester is also preferably an itaconic acid ester, and examples thereof include ethylene glycol diitaconate, propylene glycol diitaconate, 1,3-butanediol diitaconate, 1,4-butanediol diitaconate, tetramethylene glycol diitaconate, pentaerythritol diitaconate, and sorbitol tetrataconate. Examples of the crotonic acid ester include ethylene glycol dicrotonate, tetramethylene glycol dicrotonate, pentaerythritol dicrotonate, and sorbitol tetradicrotonate. Examples of the isocrotonic acid ester include ethylene glycol diisocrotonate, pentaerythritol diisocrotonate, and sorbitol tetrakisocrotonate.

Examples of the maleic acid ester include ethylene glycol dimaleate, triethylene glycol dimaleate, pentaerythritol dimaleate, and sorbitol tetramaleate.

Specific examples of the ester monomer of an aliphatic polyhydric alcohol compound with an unsaturated carboxylic acid include, as the (meth)acrylic acid ester, ethylene glycol diacrylate, triethylene glycol diacrylate, 1,3-butanediol diacrylate, tetramethylene glycol diacrylate, propylene glycol diacrylate, neopentyl glycol diacrylate, trimethylolpropane triacrylate, trimethylolpropane tri(acryloyloxypropyl) ether, trimethylolethane triacrylate, hexanediol diacrylate, 1,4-cyclohexanediol diacrylate, tetraethylene glycol diacrylate, tricyclodecanedimethanol diacrylate, tricyclodecanedimethanol dimethacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol diacrylate, dipentaerythritol hexaacrylate, tricyclodecanedimethanol diacrylate, sorbitol triacrylate, sorbitol tetraacrylate, sorbitol pentaacrylate, sorbitol hexaacrylate, tri(acryloyloxyethyl) isocyanurate, polyester acrylate oligomer, and EO-modified or PO-modified products of these compounds.

Among these, dipentaerythritol hexaacrylate and tricyclodecane dimethanol diacrylate are preferred, and tricyclodecane dimethanol diacrylate is more preferred.

Other preferred examples of the ester include aliphatic alcohol esters described in JP-B-51-47334 and JP-A-57-196231, those having an aromatic framework described in JP-A-59-5240, JP-A-59-5241 and JP-A-2-226149, and those having an amino group described in JP-A-1-165613. These ester monomers may be used also as a mixture.

Specific examples of the amide monomer of an aliphatic polyvalent amine compound with an unsaturated carboxylic acid include methylenebis-acrylamide, methylenebis-methacrylamide, 1,6-hexamethylenebis-acrylamide, 1,6-hexamethylenebis-methacrylamide, diethylenetriaminetrisacrylamide, xylylenebisacrylamide, and xylylenebismethacrylamide. Other preferred examples of the amide-based monomer include those having a cyclohexylene structure described in JP-B-54-21726.

An addition-polymerizable urethane-based compound produced by an addition reaction of an isocyanate to a hydroxyl group is also preferred, and specific examples thereof include a vinyl urethane compound having two or more polymerizable vinyl groups per molecule obtained by adding a hydroxyl group-containing vinyl monomer represented by the following formula (E) to a polyisocyanate compound having two or more isocyanate groups per molecule described in JP-B-48-41708.



[wherein each of R^4 and R^5 independently represents H or CH_3].

Furthermore, urethane acrylates described in JP-A-51-37193, JP-B-2-32293 and JP-B-2-16765 and urethane compounds having an ethylene oxide-based framework described in JP-B-58-49860, JP-B-56-17654, JP-B-62-39417 and JP-B-62-39418 are also preferred. In addition, when addition-polymerizable compounds having an amino structure or sulfide structure in the molecule described in JP-A-63-277653, JP-A-63-260909 and JP-A-1-105238 are used, a photopolymerizable composition very excellent in the photosensitivity speed can be obtained.

Other examples include a polyfunctional acrylate or methacrylate such as polyester acrylates described in JP-A-48-64183, JP-B-49-43191 and JP-B-52-30490, and epoxy acrylates obtained by reacting an epoxy resin with a (meth)acrylic acid. Other examples also include specific unsaturated compounds described in JP-B-46-43946, JP-B-1-40337 and JP-B-1-40336, and vinylphosphonic acid-based compounds described in JP-A-2-25493. In some cases, a perfluoroalkyl group-containing structure described in JP-A-61-22048 is suitably used. Furthermore, those introduced as photocurable monomers and oligomers in Journal of The Adhesion Society of Japan, Vol. 20, No. 7, pp. 300-308 (1984) may be also used.

In the present invention, when a radical polymerizable compound is added as a monomer, a polyfunctional polymerizable compound containing from two to six ethylenically unsaturated bonds is preferably used, and it is more preferred to contain from 2 to 4 ethylenically unsaturated bond. Above all, the compound preferably contains two (meth)acrylic acid ester structures.

Furthermore, in view of curing sensitivity and developability of the unexposed area, a compound containing an EO-modified product is preferred, and in view of curing sensitivity and strength of the exposed area, a compound containing a urethane bond is preferably used. In addition, in view of developability at the pattern formation, a compound having an acid group is preferably used.

Moreover, ethylenically unsaturated compounds having an acid group are also preferred, and examples of the commercially available product thereof include TO-756 that is a carboxyl group-containing trifunctional acrylate produced by Toagosei Co., Ltd., and TO-1382 that is a carboxyl group-containing pentafunctional acrylate.

In addition, examples of the highly heat-resistant polymerizable compound include

benzocyclobutene (BCB), bisallylnadiimide (BANI), benzoxazine, melamine and their analogues.

As the polymerizable compound, two or more kinds of compounds can be used.

The content of the polymerizable compound is preferably from 3 to 80 mass%, more preferably from 5 to 50 mass%, based on the entire solid content by mass of the polymerizable composition of the present invention.

Incidentally, the polymerizable compound may be the same as or different from the alkali-soluble binder.

More specifically, in the case where the polymerizable compound is a polymer, the polymerizable compound may be the same as the alkali-soluble binder described in detail later (that is, the polymerizable compound and the alkali-soluble binder may be the same component). In this embodiment, the content of the polymerizable compound is preferably from 3 to 80 mass%, more preferably from 5 to 60 mass%, based on the entire solid content by mass of the polymerizable composition of the present invention.

[3] Tungsten Compound

The polymerizable composition of the present invention contains a tungsten compound.

The tungsten compound is an infrared-blocking material exhibiting high absorption for infrared ray (light at a wavelength of about 800 to 1,200 nm) (that is, the light-blocking effect (shielding property) for infrared ray is high) and low absorption for visible light. Therefore, according to the polymerizable composition of the present invention, by virtue of containing a tungsten compound, a pattern having a high light-blocking effect in the infrared region and high light transparency in the visible region can be formed.

Also, the tungsten compound exhibits small absorption for light at a shorter wavelength than the visible region, which is employed for image formation and used at the exposure to high-pressure mercury lamp, KrF, ArF or the like. Therefore, by combining the tungsten compound with the polymerizable compound and the alkali-soluble binder, a pattern with excellent resolution is obtained by alkali development.

The tungsten compound includes, for example, a tungsten oxide-based compound, a tungsten boride-based compound and a tungsten sulfide-based compound and is preferably a tungsten oxide-based compound represented by the following formula (compositional formula) (I):



wherein M represents a metal, W represents tungsten, O represents oxygen,

$0.001 \leq x/y \leq 1.1$, and

$2.2 \leq z/y \leq 3.0$.

The metal of M includes an alkali metal, an alkaline earth metal, Mg, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Al, Ga, In, Tl, Sn, Pb, Ti, Nb, V, Mo, Ta, Re, Be, Hf, Os and Bi and is preferably an alkali metal. The metal of M may be one kind of a metal or two or more kinds of metals.

M is preferably an alkali metal, more preferably Rb or Cs, still more preferably Cs.

When x/y is 0.001 or more, the infrared ray can be sufficiently blocked, and when it is 1.1 or less, production of an impurity phase in the tungsten compound can be more unfaillingly avoided.

When z/y is 2.2 or more, chemical stability as the material can be more enhanced, and when it is 3.0 or less, the infrared ray can be sufficiently blocked.

Specific examples of the tungsten oxide-based compound represented by formula (I) include $Cs_{0.33}WO_3$, $Rb_{0.33}WO_3$, $K_{0.33}WO_3$ and $Ba_{0.33}WO_3$. The compound is preferably $Cs_{0.33}WO_3$ or $Rb_{0.33}WO_3$, more preferably $Cs_{0.33}WO_3$.

The tungsten compound is preferably a fine particle. The average particle diameter of the tungsten fine particle is preferably 800 nm or less, more preferably 400 nm or less, still more preferably 200 nm or less. When the average particle diameter is in this range, the tungsten fine particle is scarcely allowed to block the visible light because of light scattering, so that light transparency in the visible region can be more successfully ensured. From the standpoint of avoiding light scattering, the average particle diameter is preferably smaller, but for the reason of easy handling or the like at the production, the average particle diameter of the tungsten fine particle is usually 1 nm or more.

As the tungsten compound, two or more kinds of compounds may be used.

The tungsten compound is available as a commercial product but when the tungsten compound is, for example, a tungsten oxide-based compound, the tungsten oxide-based compound can be obtained by a method of heat-treating a tungsten compound in an inert gas atmosphere or a reducing gas atmosphere (see, Japanese Patent 4,096,205).

The tungsten oxide-based compound is also available, for example, as a tungsten fine particle dispersion such as YMF-02 produced by Sumitomo Metal Industries, Ltd.

The content of the tungsten compound is preferably from 3 to 20 mass%, more preferably from 5 to 15 mass%, based on the entire solid content by mass of the polymerizable composition of the present invention.

[4] Alkali-Soluble Binder

The polymerizable composition of the present invention contains an alkali-soluble binder (alkali-soluble resin). Thanks to this binder, when exposure is performed to form a pattern in the film obtained from the polymerizable composition, the unexposed area can be removed with an alkali developer, and an excellent pattern can be formed by alkali development.

The alkali-soluble binder is not particularly limited as long as it is alkali-soluble, and an appropriate alkali-soluble binder may be selected according to the purpose, but examples thereof include a (meth)acrylic resin, a urethane-based resin, polyvinyl alcohol, polyvinylbutyral, polyvinylformal, polyamide and polyester, with a (meth)acrylic resin being preferred.

The alkali-soluble binder preferably has an acid group.

Examples of the acid group include a carboxyl group, a sulfonic acid group, a phosphonic acid group, a phosphoric acid group, a sulfonamide group, a phenolic hydroxyl group and a thiol group. In view of availability of the raw material, a carboxyl group is preferred, and from the standpoint that a photosensitive layer having a shape successfully following the uneven shape of the substrate can be unfailingly formed, the acid group is preferably a phenolic hydroxyl group or a thiol group, more preferably a phenolic hydroxyl group.

The acid group-containing alkali-soluble binder is not particularly limited but is preferably a polymer obtained by using, as a monomer component, a polymerizable compound having an acid group.

The polymerizable compound having an acid group is not particularly limited and may be appropriately selected according to the purpose, and examples thereof include acrylic acid, methacrylic acid, itaconic acid, crotonic acid, isocrotonic acid, maleic acid, p-carboxystyrene and p-hydroxystyrene. Among these, acrylic acid, methacrylic acid, p-carboxystyrene and p-hydroxystyrene are preferred, and p-hydroxystyrene is most preferred. Here, the polymer obtained using p-hydroxystyrene is a polymer having a phenolic hydroxyl group as the acid group. Examples of the alkali-soluble binder having a phenolic hydroxyl

group include MARUKA LYNCUR M, MARUKA LYNCUR MB (product names, produced by Maruzen Petrochemical Co., Ltd.), VP-2500, and VP-12000 (p-vinylphenol polymer, product names, produced by Nippon Soda Co., Ltd.).

The acid dissociation constant pK_a of the polymerizable group having such an acid group is preferably from 4.0 to 11.0, more preferably from 6.0 to 11.0, still more preferably from 8.0 to 11.0.

The acid group-free polymerizable compound is not particularly limited, but preferred examples thereof include a (meth)acrylic acid ester (such as alkyl ester, aryl ester and aralkyl ester).

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

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

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

The molar ratio between a monomer corresponding to the acid group-containing polymerizable compound and a monomer corresponding to the acid group-free polymerizable compound is usually from 1:99 to 99:1, preferably from 30:70 to 99:1, more preferably from 50:50 to 99:1.

The content of the acid group in the alkali-soluble binder is not particularly limited but is preferably from 0.5 to 4.0 meq/g, more preferably from 1.0 to 3.0 meq/g. When the content is 0.5 meq/g or more, satisfactory alkali developability is obtained and an excellent pattern can be more unfailingly obtained. Also, when the content is 4.0 meq/g or less, the fear of impairing the strength of the permanent pattern can be reliably avoided.

The alkali-soluble binder preferably further has a crosslinking group, and this is preferred particularly in that both the curability of the exposed area and alkali developability of the unexposed area can be enhanced and a pattern having high durability is obtained (in particular, when higher durability is required of the solder resist, for example, when the wiring density of the metal wiring covered with a solder resist is high, the above-described effects are prominent). The crosslinking group as used herein indicates a group capable of crosslinking

the binder polymer in the process of polymerization reaction brought about in the photosensitive layer when the photosensitive layer obtained from the polymerizable composition is exposed or heated. The crosslinking group is not particularly limited as long as it is a group having such a function, but examples of the functional group capable of undergoing an addition polymerization reaction include an ethylenically unsaturated bond group, an amino group and an epoxy group. The crosslinking group may be also a functional group capable of becoming a radical upon irradiation with light, and examples of such a crosslinking group include a thiol group and a halogen group. Above all, an ethylenically unsaturated bond group is preferred. The ethylenically unsaturated bond group is preferably a styryl group, a (meth)acryloyl group or an allyl group, and from the standpoint of satisfying both the stability of the crosslinking group before exposure and the strength of the permanent pattern, a (meth)acryloyl group is more preferred.

For example, a free radical (a polymerization initiating radical or a radical grown in the polymerization process of a polymerizable compound) is added to the crosslinking functional group of the alkali-soluble binder to cause addition polymerization between polymers directly or through a polymerization chain of the polymerizable compound, as a result, crosslinking is formed between polymer molecules and curing is thereby effected. Alternatively, an atom (for example, a hydrogen atom on the carbon atom adjacent to the functional crosslinkable group) in the polymer is withdrawn by a free radical to produce a polymer radical, and the polymer radicals combine with each other to form crosslinking between polymer molecules, thereby effecting curing.

The content of the crosslinkable group in the alkali-soluble binder is not particularly limited but is preferably from 0.5 to 3.0 meq/g, more preferably from 1.0 to 3.0 meq/g, still more preferably from 1.5 to 2.8 meq/g. When the content is 0.5 meq/g or more, the amount of curing reaction is sufficiently large and high sensitivity is obtained, and when 3.0 meq/g or less, storage stability of the polymerizable composition can be enhanced.

The content (meq/g) above can be measured, for example, by iodine value titration.

The alkali-soluble binder having a crosslinking group is described in detail in JP-A-2003-262958, and compounds described in this publication can be used also in the present invention.

The alkali-soluble binder having a crosslinking group is preferably an alkali-soluble binder having an acid group and a crosslinking group, and representative examples thereof are the followings:

(1) a urethane-modified polymerizable double bond-containing acrylic resin obtained by reacting a compound which has one unreacted isocyanate group allowed to remain after previously reacting an isocyanate group and an OH group and contains at least one (meth)acryloyl group, with a carboxyl group-containing acrylic resin;

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

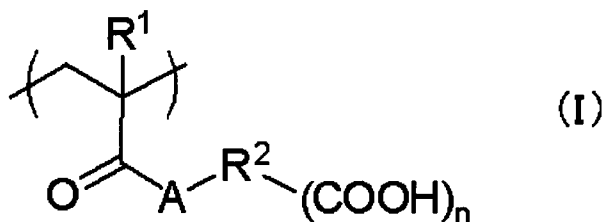
(3) a polymerizable double bond-containing acrylic resin obtained by reacting an OH group-containing acrylic resin with a dibasic acid anhydride having a polymerizable double bond.

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

The alkali-soluble binder having an acid group and a crosslinking group also includes, for example, a polymer compound having an acidic group and an ethylenically unsaturated bond in the side chain and having a bisphenol A-type framework and a bisphenol F-type framework, a novolak resin having an acidic group and an ethylenically unsaturated bond, and a resol resin. These resins can be obtained by the technique described in paragraphs [0008] to [0027] of JP-A-11-240930.

As described above, the alkali-soluble binder is preferably a (meth)acrylic resin, and the "(meth)acrylic resin" is preferably a copolymer having, as a polymerization component, a (meth)acrylic acid derivative such as (meth)acrylic acid, (meth)acrylic acid ester (e.g., alkyl ester, aryl ester, aralkyl ester), (meth)acrylamide and (meth)acrylamide derivative.

The (meth)acrylic resin is preferably, for example, a copolymer having an acid group-containing repeating unit. Preferred examples of the acid group include those described above. As the acid group-containing repeating unit, a (meth)acrylic acid-derived repeating unit or a repeating unit represented by the following formula (I) is preferably used.



(In formula (I), R^1 represents a hydrogen atom or a methyl group, R^2 represents a single bond or an $n+1$ -valent linking group, A represents an oxygen atom or $-\text{NR}^3$ -, R^3 represents a hydrogen atom or a monovalent hydrocarbon group having a carbon number of 1 to 10, and n represents an integer of 1 to 5.)

The linking group represented by R^2 in formula (I) is preferably composed of one or more atoms selected from the group consisting of a hydrogen atom, a carbon atom, an oxygen atom, a nitrogen atom, a sulfur atom and a halogen atom, and the number of atoms constituting the linking groups represented by R^2 is preferably from 1 to 80. Specific examples of the linking group include an alkylene group and an arylene group, and the linking group may have a structure where a plurality of divalent linking groups described above are connected through any one of an amide bond, an ether bond, a urethane bond, a urea bond and an ester bond. R^2 is preferably a single bond, an alkylene group, or a structure where a plurality of alkylene groups are connected through at least one of an amide bond, an ether bond, a urethane bond, a urea bond and an ester bond.

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

The carbon number of the arylene group is preferably from 6 to 14, more preferably from 6 to 10.

The alkylene group and arylene group may further have a substituent, and examples of the substituent include a monovalent nonmetallic atom group excluding hydrogen atom and include a halogen atom (-F, -Br, -Cl, -I), a hydroxyl group, a cyano group, an alkoxy group, an aryloxy group, a mercapto group, an alkylthio group, an arylthio group, an alkylcarbonyl group, an arylcarbonyl group, a carboxyl group and its conjugate base group, an alkoxycarbonyl group, an aryloxycarbonyl group, a carbamoyl group, an aryl group, an alkenyl group, and an alkynyl group.

The hydrocarbon group of R^3 preferably has a carbon number of 1 to 10, more preferably from 1 to 5, still more preferably from 1 to 3.

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

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

The ratio (mol%) of the acid group-containing repeating unit occupying in all repeating unit components of the (meth)acrylic resin is, in view of developability, preferably from 10 to 90%, and in view of satisfying both developability and strength of the permanent pattern, the ratio is more preferably from 50 to 85%, still more preferably from 60 to 80%.

As already stated, the (meth)acrylic resin preferably further has a crosslinking group, and specific examples and content of the crosslinking group are the same as those described above.

The (meth)acrylic polymer for use in the present invention may contain, in addition

to the acid group-containing polymerization unit and the crosslinking group-containing polymerization unit, a polymerization unit of (meth)acrylamide or a derivative thereof, a polymerization unit of α -hydroxymethyl acrylate, and a polymerization unit of styrene derivative. The alkyl group of the (meth)acrylic acid alkyl ester is preferably an alkyl group having a carbon number of 1 to 5 or an alkyl group with the above-described substituent having a carbon number of 2 to 8, more preferably a methyl group. Examples of the (meth)acrylic acid aralkyl ester include benzyl (meth)acrylate. Examples of the (meth)acrylamide derivative include N-isopropylacrylamide, N-phenylmethacrylamide, N-(4-methoxycarbonylphenyl)methacrylamide, N,N-dimethylacrylamide, and morpholinoacrylamide. Examples of the α -hydroxymethyl acrylate include ethyl α -hydroxymethylacrylate and cyclohexyl α -hydroxymethylacrylate. Examples of the styrene derivative include styrene and 4-tert-butylstyrene.

As the alkali-soluble binder other than the (meth)acrylic resin, an acetal-modified polyvinyl alcohol-based binder polymer having an acid group described, for example, in European Patents 993,966 and 1,204,000 and JP-A-2001-318463 is preferred because of excellent balance between film strength and developability. In addition, a water-soluble linear organic polymer such as polyvinylpyrrolidone and polyethylene oxide is useful. Also, an alcohol-soluble nylon, a polyether of 2,2-bis-(4-hydroxyphenyl)-propane and epichlorohydrin, and the like are useful for increasing the strength of the cured film.

Above all, a [benzyl (meth)acrylate/(meth)acrylic acid/if desired, another addition-polymerizable vinyl monomer] copolymer, and a [allyl (meth)acrylate/(meth)acrylic acid/if desired, another addition-polymerizable vinyl monomer] copolymer are preferred because of excellent balance among film strength, sensitivity and developability.

The weight average molecular weight of the binder polymer which can be used in the polymerizable composition of the present invention is preferably 3,000 or more, more preferably from 5,000 to 300,000, and most preferably from 10,000 to 30,000, and the number average molecular weight is preferably 1,000 or more, more preferably from 2,000 to 250,000. The polydispersity (weight average molecular weight/number average molecular weight) is preferably 1 or more, more preferably from 1.1 to 10.

The binder polymer may be any of a random polymer, a block polymer, a graft polymer and the like.

The alkali-soluble binder can be synthesized by a conventionally known method. Examples of the solvent used at the synthesis include tetrahydrofuran, ethylene dichloride,

cyclohexanone, propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, and butyl acetate. One of these solvents may be used alone, or two or more thereof may be mixed and used.

One of these alkali-soluble binders may be used alone, or two or more thereof may be used in combination.

The content of the alkali-soluble binder is preferably from 5 to 80 mass%, more preferably from 30 to 60 mass%, based on the entire solid content by mass of the polymerizable composition of the present invention. With a content in this range, the exposure sensitivity is good, the processing time can be short, and good TCT resistance is obtained.

[5] Inorganic filler

The polymerizable composition of the present invention contains an inorganic filler as an essential component. The operation mechanism is not clearly known, but it is considered that by containing an inorganic filler in the polymerizable composition of the present invention, when the substrate on which a photosensitive layer is formed has an uneven shape, the polymerizable composition can form a photosensitive layer having a shape successfully following the uneven shape of the substrate.

For example, as shown in the schematic cross-sectional view of Fig. 11, a photosensitive layer 503 formed of the polymerizable composition is formed on a substrate having an uneven shape (hereinafter, sometimes referred to as an "uneven substrate"), that is, a substrate where a plurality of wirings (for example, copper wiring) 502 are provided with a wiring-to-wiring distance W on the surface 501a of a silicon substrate 501.

Here, the photosensitive layer 503 is formed by coating a solution of the polymerizable composition on a support and, if desired, heat-treating the coating. At this time, particularly when the wiring-to-wiring distance W of the plurality of wirings 502 is small (in particular, when the wiring-to-wiring distance W is 100 μm or less), although the thickness of the photosensitive layer provided on the wiring surface 502a is the desired thickness, the thickness of the photosensitive layer in the inter-wiring region C is sometimes greatly larger than the desired thickness. More specifically, the dotted line part in the inter-wiring region C of Fig. 11 indicates a state where the distance between the bottom C2 of the photosensitive layer surface in the inter-wiring region C and the surface 501a of the silicon substrate 501, that is, the thickness t2 of the photosensitive layer in the inter-wiring region C, is greatly larger

than the desired thickness. This is presumed to be ascribable to the fact that at the time of, for example, drying the solvent from the coating layer of the polymerizable composition provided on the substrate, the surface of the coating layer in the inter-wiring region C rises.

However, in the photosensitive layer formed of the polymerizable composition of the present invention, the thickness of the photosensitive layer in the inter-wiring region C is close to the desired thickness. More specifically, in this case, the distance between the bottom C1 of the photosensitive layer surface in the inter-wiring region C and the surface 501a of the silicon substrate 501, that is, the thickness $t1$ of the photosensitive layer in the inter-wiring region C, is close to the desired thickness. This is presumed to result because the inorganic filler contained in the polymerizable composition of the present invention keeps the coating layer surface in the inter-wiring region C from rising at the time of, for example, drying the solvent from the coating layer of the polymerizable composition provided in the inter-wiring region. In this way, according to the polymerizable composition of the present invention can form a photosensitive layer having a shape successfully following the uneven surface of the substrate.

According to the polymerizable composition of the present invention, since the thickness of the photosensitive layer in the inter-wiring region C is close to the desired thickness, when the inter-wiring region C is included in the exposure region, light such as radiation in the exposure step can reliably reach the deep part of the photosensitive layer in the inter-wiring region C (for example, the site near the surface 501a of the silicon substrate 501, in the photosensitive layer), and sufficient curing by exposure can be achieved. As a result, the fear of causing separation of the pattern or generation of an adherence failure to the substrate on the uneven substrate can be reduced.

The inorganic filler which can be used in the present invention is preferably silica, more preferably spherical silica surface-treated with a silane coupling agent.

The polymerizable composition of the present preferably contains a filler, and this is preferred in that a pattern having high durability is obtained (the effect is prominent particularly when higher durability is required of the solder resist, for example, when the wiring density of the metal wiring covered with a solder resist is high).

By virtue of using spherical silica surface-treated with a silane coupling agent, the thermal cycle test resistance and storage stability of the polymerizable composition are enhanced, and the same good profile as that immediately after pattern formation can be maintained even after experiencing, for example, a severe atmosphere such as thermal cycle

test.

The term "spherical" in the spherical filler may be sufficient if the particle is not of a needle-like, columnar or amorphous shape but is rounded, and the shape need not be necessarily "truly spherical". However, the typical "spherical" shape is "a truly spherical" shape.

Whether the filler is spherical can be confirmed by observing it through a scanning electron microscope (SEM).

The volume average primary particle diameter of the inorganic filler is not particularly limited and may be appropriately selected according to the purpose but is preferably from 0.05 to 3 μm , more preferably from 0.1 to 1 μm . When the volume average primary particle diameter of the filler is in the range above, this is advantageous in that impairment of the processability due to development of thixotropy is suppressed and the maximum particle diameter is kept from becoming large, as a result, generation of a defect ascribable to attachment of an extraneous material to the cured film obtained or non-uniformity of the coated film can be prevented.

The volume average primary particle diameter of the inorganic filler can be measured by a dynamic light scattering particle diameter distribution measuring apparatus.

The inorganic filler can be dispersed using the above-described dispersant and binder. As stated above, in view of curability, an alkali-soluble binder having a crosslinking group in the side chain is preferred.

-Surface Treatment-

The surface treatment of the inorganic filler is described below. The surface treatment of the inorganic filler is not particularly limited and may be appropriately selected according to the purpose, but a treatment of covering silica with a silane coupling agent is preferred.

-Silane Coupling Agent-

The silane coupling agent used for the surface treatment of the inorganic filler is not particularly limited and may be appropriately selected according to the purpose, but a silane coupling agent containing at least one functional group selected from an alkoxysilyl group, a chlorosilyl group and an acetoxysilyl group (hereinafter, sometimes referred to as a "first functional group") and at least one functional group selected from a (meth)acryloyl group, an amino group and an epoxy group (hereinafter, sometimes referred to as a "second functional group") is preferred. The second functional group is more preferably a (meth)acryloyl group

or an amino group, and it is still more preferred that the second functional group is a (meth)acryloyl group. When the second functional group is a (meth)acryloyl group, this is advantageous in view of storage stability and TCT resistance.

A coupling agent containing, as a first functional group, at least one member selected from an alkoxysilyl group, a chlorosilyl group and an acetoxysilyl group and, as a second functional group, at least one member selected from an imidazole group, an alkylimidazole group and a vinylimidazole group, described in JP-B-7-68256, can be also preferably used.

The silane coupling agent is not particularly limited, but preferred examples thereof include a γ -aminopropyltriethoxysilane, N-(β -aminoethyl)- γ -aminopropyltrimethoxysilane, N-(β -aminoethyl)- γ -aminopropylmethyldimethoxysilane, γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropylmethyldimethoxysilane, γ -methacryloxypropyltriethoxysilane, γ -methacryloxypropylmethyldimethoxysilane, α -[[3-(trimethoxysilyl)propoxy]methyl]-imidazole-1-ethanol described in JP-B-7-68256, 2-ethyl-4-methyl- α -[[3-(trimethoxysilyl)propoxy]methyl]-imidazole-1-ethanol, 4-vinyl- α -[[3-(trimethoxysilyl)propoxy]methyl]-imidazole-1-ethanol, 2-ethyl-4-methylimidazopropyltrimethoxysilane, and their salts, intramolecular condensates and intermolecular condensates. One kind of these compounds may be used alone, or two or more kinds thereof may be used in combination.

The surface treatment of spherical silica with the silane coupling agent may be previously performed only for the spherical silica (in this case, hereinafter, sometimes referred to as a "pretreatment") or may be performed together with a part or all of other fillers contained in the polymerizable composition.

The method for performing the pretreatment is not particularly limited, and examples of the method include a dry method, an aqueous solution method, an organic solvent method and a spray method. The temperature at which the pretreatment is performed is not particularly limited but is preferably from normal temperature to 200°C.

It is also preferred to add a catalyst when performing the pretreatment. The catalyst is not particularly limited, and examples thereof include an acid, a base, a metal compound, and an organic metal compound.

In the case of performing the pretreatment, the amount of the silane coupling agent added is not particularly limited but is preferably from 0.01 to 50 parts by mass, more preferably from 0.05 to 50 parts by mass, per 100 parts by mass of the spherical silica. When

the amount added is in this range, a surface treatment enough to develop the effect is performed and at the same time, reduction in the handleability due to aggregation of spherical silica after treatment is suppressed.

The above-described silane coupling agent has an action of enhancing the adherence between the base material and the photosensitive layer, because the first functional group reacts with an active group in the base material surface, spherical silica surface and binder and the second functional group reacts with a carboxyl group and an ethylenically unsaturated group of the binder. On the other hand, the silane coupling agent has high reactivity and if the silane coupling agent itself is added to the polymerizable composition, mainly the second functional group sometimes undergoes reaction or deactivation during storage due to the diffusion action, giving rise to reduction in the shelf life or pot life.

However, when spherical silica pretreated with a silane coupling agent is used, the diffusion action is suppressed to greatly improve the problem of shelf life or pot life, and it becomes possible to take even a one-liquid system. Furthermore, in the case of applying the pretreatment to spherical silica, the conditions such as stirring condition, temperature condition and use of catalyst can be freely selected, so that compared to the addition without applying the pretreatment, the reaction ratio of the first functional group of the silane coupling agent with an active group in the spherical silica can be significantly increased. Accordingly, very good results are obtained in terms of required characteristics under severe conditions such as electroless gold plating, electroless solder plating and moisture resistance load test. Also, by performing the pretreatment, the amount of the silane coupling agent used can be decreased, and the shelf life and pot life can be more improved.

Examples of the spherical silica surface-treated with a silane coupling agent, which can be used in the present invention, include FB and SFP Series of Denki Kagaku Kogyo Kabushiki Kaisha; 1-FX of Tatsumori Ltd.; HSP Series of Toagosei Co., Ltd.; and SP Series of Fuso Chemical Co., Ltd.

The content of the inorganic filler is preferably from 1 to 60 mass%, more preferably from 20 to 60 mass%, still more preferably from 40 to 60 mass%, based on the entire solid content by mass of the polymerizable composition. When the amount added is in this range, in the case where the substrate on which the photosensitive layer is provided has an uneven shape, a photosensitive layer having a shape successfully following the uneven shape of the substrate can be more unfailingly formed.

[6] Ultraviolet Absorber

It is preferable that the polymerizable composition of the present invention contain an ultraviolet absorber.

The ultraviolet absorber is incorporated, for example, into a resist composition for solder resists and after forming a photosensitive layer by coating the resist composition on a semiconductor substrate for solid-state imaging devices, where an alignment mark is provided on the surface, exposure and development are performed to form a solder resist layer, whereby a solder resist layer capable of satisfying both elimination of the later-described "problem attributable to reflected light on the substrate surface" and unfailing detection of the alignment mark by a visible light sensor can be more reliably produced.

In the case where the substrate surface having provided thereon a photosensitive layer is formed of a material having high light reflectivity, such as metal, the cross-sectional shape of the obtained pattern is liable to become a skirt shape (that is, rectangularity of the cross-sectional shape is liable to be impaired), since reflected light from the substrate surfactant in exposure to the photosensitive layer becomes considerable. On the other hand, in the case, if the exposure dose is kept low so as to reduce the reflected light, a pattern having a rectangular cross-sectional shape can be hardly formed due to insufficient exposure dose.

However, in the case where the polymerizable composition of the present invention contains the ultraviolet absorber, even when irradiation is performed with an exposure dose necessary to obtain a pattern having a rectangular cross-sectional shape (hereinafter, sometimes referred to as an "adequate exposure dose"), the ultraviolet absorber absorbs the reflected light and this makes it easy to form a pattern having a rectangular cross-sectional shape.

The ultraviolet absorber is preferably a compound incapable of initiating the polymerization of a polymerizable compound by light or heat (that is, a compound not coming under the polymerization initiator). The expression "incapable of initiating the polymerization of a polymerizable compound" as used herein means that even when the ultraviolet absorber receives light or heat energy, it does not generate an active species for initiating the polymerization of a polymerizable compound.

To be more specific, the ultraviolet absorber is preferably a compound having no photosensitivity to ultraviolet or visible ray (more specifically, light at a wavelength of 300 to 450 nm) and having no thermosensitivity to heat (more specifically, for example, heat at 150 to 250°C). The terms "photosensitivity" and "thermosensitivity" as used herein mean to

develop the objective function while involving change in the chemical structure by the effect of ultraviolet or visible ray or heat.

Furthermore, the ultraviolet absorber is preferably not only incapable of initiating the polymerization of a polymerizable compound but also lacking in the property of the sensitizer described later. The term "property of the sensitizer" as used herein indicates the property of transferring energy obtained by light absorption of the sensitizer itself to another material (polymerization initiator) and thereby initiating the polymerization.

The ultraviolet absorber is preferably a compound having a maximum absorption wavelength between 300 nm and 430 nm, more preferably a compound having a maximum absorption wavelength between 330 nm and 420 nm.

The ultraviolet absorber still more preferably has a maximum absorption wavelength at least in one range out of (I) the range of 340 to 380 nm, (II) the range of 380 to 420 nm, and (III) the range of 420 to 450 nm.

At the time of forming a pattern by applying exposure and development to the photosensitive layer formed using the polymerizable composition of the present invention, in the case where the light source for exposure contains i-line, the ultraviolet absorber preferably has a maximum absorption wavelength in the wavelength range (I) above.

In the case where the light source for exposure contains h-line, the ultraviolet absorber preferably has a maximum absorption wavelength in the wavelength range (II) above.

In the case where the light source for exposure contains g-line, the ultraviolet absorber preferably has a maximum absorption wavelength in the wavelength range (III) above.

As the ultraviolet absorber, for example, a salicylate-based, benzophenone-based, benzotriazole-based, substituted acrylonitrile-based or triazine-based ultraviolet absorber may be used.

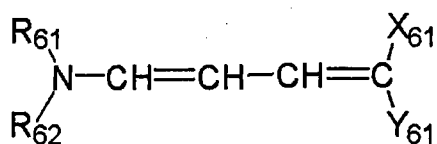
Examples of the salicylate-based ultraviolet absorber include phenyl salicylate, p-octylphenyl salicylate and p-tert-butylphenyl salicylate. Examples of the benzophenone-based ultraviolet absorber include 2,2'-dihydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, 2,2',4,4'-tetrahydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2,4-dihydroxybenzophenone and 2-hydroxy-4-octoxybenzophenone. Examples of the benzotriazole-based ultraviolet absorber include 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3'-tert-amyl-5'-isobutylphenyl)-5-chlorobenzotriazole, 2-

(2'-hydroxy-3'-isobutyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3'-isobutyl-5'-propylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)benzotriazole, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, and 2-[2'-hydroxy-5'-(1,1,3,3-tetramethyl)phenyl]benzotriazole.

Examples of the substituted acrylonitrile-based ultraviolet absorber include ethyl 2-cyano-3,3-diphenylacrylate and 2-ethylhexyl 2-cyano-3,3-diphenylacrylate. Examples of the triazine-based ultraviolet absorber include a mono(hydroxyphenyl)triazine compound such as 2-[4-[(2-hydroxy-3-dodecyloxypropyl)oxy]-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[4-[(2-hydroxy-3-tridecyloxypropyl)oxy]-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine and 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine; a bis(hydroxyphenyl)triazine compound such as 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-3-methyl-4-propyloxyphenyl)-6-(4-methylphenyl)-1,3,5-triazine and 2,4-bis(2-hydroxy-3-methyl-4-hexyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine; and a tris(hydroxyphenyl)triazine compound such as 2,4-bis(2-hydroxy-4-butoxyphenyl)-6-(2,4-dibutoxyphenyl)-1,3,5-triazine, 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine and 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxypropyloxy)phenyl]-1,3,5-triazine.

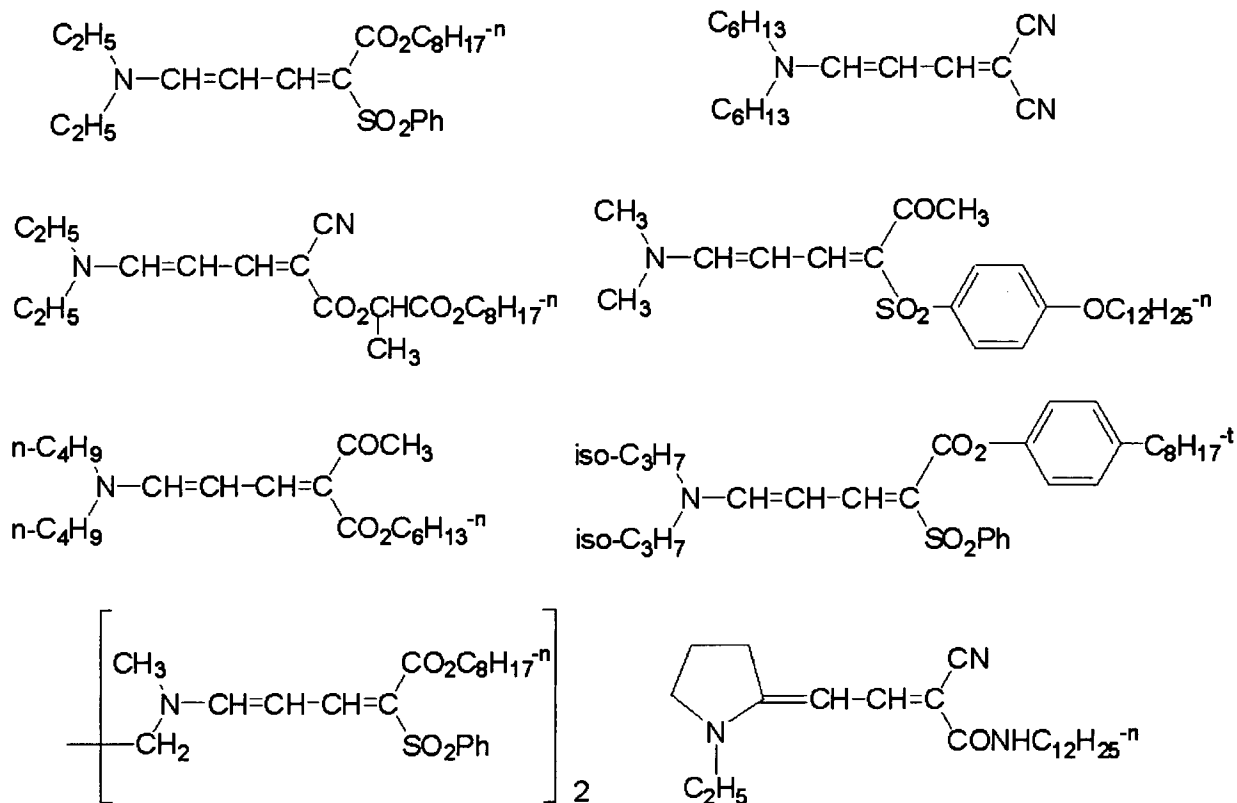
The ultraviolet absorber is preferably a compound represented by the following formula (A):

Formula (A):



In the formula, each of R_{61} and R_{62} independently represents a hydrogen atom, an alkyl group, an aryl group, or a nonmetallic atom group necessary for forming a 5- or 6-membered ring by combining with each other. Also, either one of R_{61} and R_{62} may combine with the methine group next to the nitrogen atom to form a 5- or 6-membered ring. Each of X_{61} and Y_{61} independently represents a cyano group, $-\text{COOR}_{63}$, $-\text{CONR}_{63}\text{R}_{64}$, $-\text{COR}_{63}$, $-\text{SO}_2\text{R}_{63}$ or $-\text{SO}_2\text{R}_{63}\text{R}_{64}$, and each of R_{63} and R_{64} independently represents a hydrogen atom, an alkyl group or an aryl group. X_{61} and Y_{61} may combine with each other to form a 5- or 6-membered ring. Furthermore, any one of R_{61} , R_{62} , X_{61} and Y_{61} may combine with any one of R_{61} , R_{62} , X_{61} and Y_{61} in another compound represented by formula (A) to form a dimer.

Specific examples of the compound represented by formula (A) are illustrated below, but the present invention is not limited thereto.



In the present invention, one of these various ultraviolet absorbers may be used alone, or two or more thereof may be used in combination.

The polymerizable composition of the present invention may or may not contain the ultraviolet absorber but in the case of containing the ultraviolet absorber, the content thereof is preferably from 0.001 to 1 mass%, more preferably from 0.01 to 0.3 mass%, based on the entire solid content by mass of the polymerizable composition of the present invention.

[6] Infrared-blocking material other than tungsten compound

The polymerizable composition of the present invention may contain an infrared-blocking material other than a tungsten compound and a metal boride (hereinafter, sometimes referred to as "the other infrared-blocking material") within the range not impairing the effects of the present invention. The other infrared-blocking material is preferably a compound having absorption at a wavelength of 800 to 1,200 nm and exhibiting good transparency to light used for exposure, and from such viewpoints, the other infrared-blocking material is preferably selected from infrared-absorbing dyestuffs and infrared-absorbent inorganic pigments.

Examples of the infrared-absorbing dyestuff include a cyanine dye, a phthalocyanine dye, a naphthalocyanine dye, an immonium dye, an aminium dye, a quinolium dye, a pyrylium dye, and a metal complex dye such as Ni complex dye.

The dye usable as the infrared-blocking material is also available as a commercial product, and preferred examples thereof include the following commercially available dyes:

S0345, S0389, S0450, S0253, S0322, S0585, S0402, S0337, S0391, S0094, S0325, S0260, S0229, S0447, S0378, S0306 and S0484 produced by FEW Chemicals;

ADS795WS, ADS805WS, ADS819WS, ADS820WS, ADS823WS, ADS830WS, ADS850WS, ADS845MC, ADS870MC, ADS880MC, ADS890MC, ADS920MC, ADS990MC, ADS805PI, ADSW805PP, ADS810CO, ADS813MT, ADS815EI, ADS816EI, ADS818HT, ADS819MT, ADS819MT, ADS821NH, ADS822MT, ADS838MT, ADS840MT, ADS905AM, ADS956BP, ADS1040P, ADS1040T, ADS1045P, ADS1040P, ADS1050P, ADS1065A, ADS1065P, ADS1100T and ADS1120F produced by American Dye Source, Inc.;

YKR-4010, YKR-3030, YKR-3070, MIR-327, MIR-371, SIR-159, PA-1005, MIR-369, MIR-379, SIR-128, PA-1006, YKR-2080, MIR-370, YKR-3040, YKR-3081, SIR-130, MIR-362, YKR-3080, SIR-132 and PA-1001 produced by Yamamoto Chemical Industry Co., Ltd.; and

NK-123, NK-124, NK-1144, NK-2204, NK-2268, NK-3027, NKX-113, NKX-1199, NK-2674, NK-3508, NKX-114, NK-2545, NK-3555, NK-3509 and NK-3519 produced by Hayashibara Biochemical Labs, Inc.

Among these dyes, in view of heat resistance, a phthalocyanine dye and a metal complex dye are preferred.

One of these dyes may be used alone, or for the purpose of bringing out good light-blocking effect at a wavelength of 800 to 1,200 nm, two or more dyes according to this purpose may be mixed and used.

Examples of the infrared-absorbent inorganic pigment which can be used as the other infrared-blocking material include zinc flower, lead white, lithopone, titanium oxide, chromium oxide, precipitating barium sulfate, barite powder, red lead, iron oxide red, lead yellow, zinc yellow (type 1 zinc yellow, type 2 zinc yellow), ultramarine blue, Prussian blue (iron/potassium ferrocyanide), zircon grey, praseodymium yellow, chrome-titanium yellow, chrome green, peacock blue, Victoria green, iron blue (irrelevant to Prussian blue), vanadium-zirconium blue, chrome-tin pink, manganese pink and salmon pink. Furthermore, as a black

pigment, for example, a metal oxide, a metal nitride or a mixture thereof each containing one metal element or two or more metal elements selected from the group consisting of Co, Cr, Cu, Mn, Ru, Fe, Ni, Sn, Ti and Ag, may be used.

The black pigment is preferably titanium black that is a titanium nitride-containing black pigment, because shielding property in the infrared region at a wavelength of 800 to 1,200 nm is good.

Titanium black can be obtained by a conventionally known method, and as the commercially available product, titanium black produced, for example, by Ishihara Sangyo Kaisha, Ltd., Ako Kasei Co., Ltd., JEMCO Inc., Mitsubishi Materials Corp., or Mitsubishi Materials Electronic Chemicals Co., Ltd. may be used.

Titanium black indicates a black particle having a titanium atom, and low-order titanium oxide, titanium oxynitride or the like is preferred. As the titanium black particle, a surface-modified particle may be used, if desired, for the purpose of improving dispersibility, preventing aggregation, or the like.

The surface modification method includes a method of covering the surface with one or more members selected from silicon oxide, titanium oxide, germanium oxide, aluminum oxide, magnesium oxide, and zirconium oxide. Also, the surface may be treated with a water-repellent substance described in paragraphs [0010] to [0027] of JP-A-2007-302836.

Examples of the method for producing titanium black include, but are not limited to, a method of reducing a mixture of titanium dioxide and metal titanium by heating it in a reductive atmosphere (JP-A-49-5432); a method of reducing ultrafine titanium dioxide obtained by high-temperature hydrolysis of titanium tetrachloride, in a reductive atmosphere containing hydrogen (JP-A-57-205322); a method of reducing titanium dioxide or titanium hydroxide at high temperature in the presence of ammonia (JP-A-60-65069, JP-A-61-201610); and a method of attaching a vanadium compound to titanium dioxide or titanium hydroxide and then reducing it at high temperature in the presence of ammonia (JP-A-61-201610).

The particle diameter of the titanium black particle is not particularly limited but in view of dispersibility and colorability, the particle diameter is preferably from 3 to 2,000 nm, more preferably from 10 to 500 nm.

The specific surface area of titanium black is not particularly limited, but usually, the value measured by the BET method is preferably on the order of 5 to 150 m²/g, more preferably on the order of 20 to 100 m²/g, because titanium black after surface treatment with a water-repellent agent can have a predetermined performance in terms of water repellency.

With respect to the particle diameter of the inorganic pigment used as the other infrared-blocking material, the average particle diameter is preferably from 3 nm to 0.01 mm, and in view of dispersibility, light-blocking effect and precipitation with aging, the average particle diameter is preferably from 10 nm to 1 μ m.

The polymerizable composition may or may not contain the other infrared-blocking material but in the case of containing the other infrared-blocking material, the content thereof is preferably from 5 to 75 mass%, more preferably from 10 to 40 mass%, based on the mass of the tungsten compound.

[7] Dispersant

In the present invention, particularly when the tungsten compound is a fine particle, the fine particle may be dispersed using a known dispersant for the purpose of enhancing the dispersibility and dispersion stability of the tungsten compound in the polymerizable composition.

As the dispersant, for example, a known dispersant or surfactant may be appropriately selected and used.

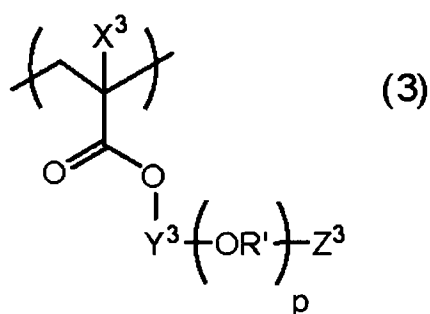
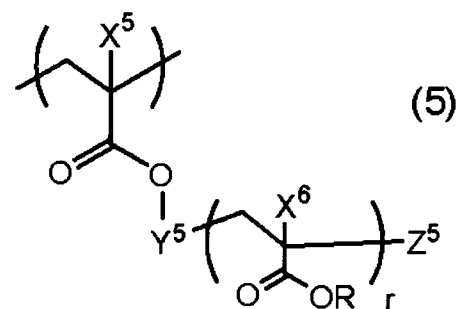
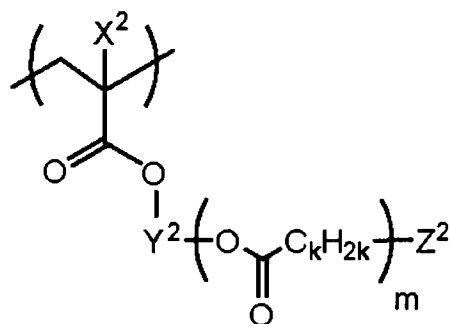
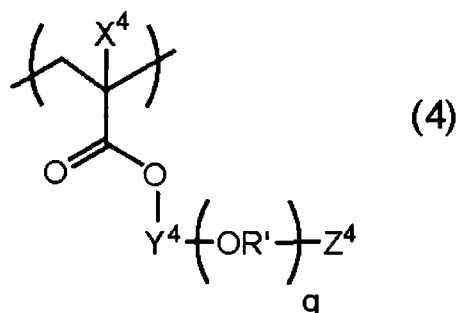
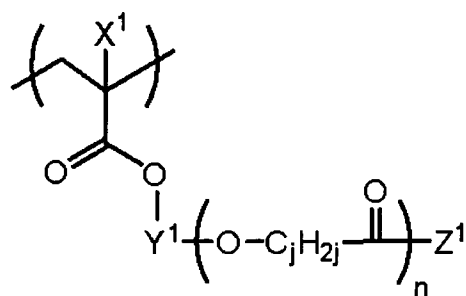
Specifically, many kinds of compounds are usable, and examples thereof include a cationic surfactant such as Organosiloxane Polymer KP341 (produced by Shin-Etsu Chemical Co.), (meth)acrylic acid-based (co)polymer Polyflow No. 75, No. 90 and No. 95 (produced by Kyoeisha Chemical Co., Ltd.), and W001 (produced by Yusho Co., Ltd.); a nonionic surfactant such as polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene nonylphenyl ether, polyethylene glycol dilaurate, polyethylene glycol distearate, and sorbitan fatty acid ester; an anionic surfactant such as W004, W005 and W017 (produced by Yusho Co., Ltd.); a polymer dispersant such as EFKA-46, EFKA-47, EFKA-47EA, EFKA POLYMER 100, EFKA POLYMER 400, EFKA POLYMER 401, EFKA POLYMER 450 (all produced by BASF Japan); various Solspersperse dispersants such as SOLSPERSE 3000, 5000, 9000, 12000, 13240, 13940, 17000, 24000, 26000, 28000, 32000 and 36000 (produced by The Lubrizol Corporation); ADEKA PLURONIC L31, F38, L42, L44, L61, L64, F68, L72, P95, F77, P84, F87, P94, L101, P103, F108, L121 and P-123 (produced by ADEKA), ISONET S-20 (produced 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 and 2150 (produced by BYK Chemie Japan). Other examples include an oligomer or

polymer having a polar group in the molecular terminal or side chain, such as acrylic copolymer.

In view of dispersibility, developability, precipitation, the following resins described in JP-A-2010-106268 are preferred, and particularly in view of dispersibility, a polymer dispersant having a polyester chain in the side chain is preferred. Also, in view of dispersibility and resolution of a pattern formed by photolithography, a resin having an acid group and a polyester chain is preferred. As the acid group in the dispersant, in view of adsorptive property, an acid group with pKa of 6 or less is preferred, and a carboxylic acid, a sulfonic acid or a phosphoric acid is more preferred.

The dispersant resin described in JP-A-2010-106268, which is preferably used in the present invention, is described below.

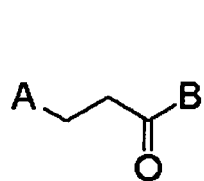
The dispersant resin is preferably a graft copolymer containing, in the molecule, a graft chain having a number of atoms, excluding hydrogen atom, of 40 to 10,000 and being selected from a polyester structure, a polyether structure and a polyacrylate structure, which is a graft copolymer containing a structural unit represented by any one of the following formulae (1) to (5).



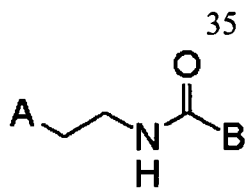
In Formulae (1) to (5), each of X^1 , X^2 , X^3 , X^4 , X^5 and X^6 independently represents a hydrogen atom or a monovalent organic group and in view of restriction in the synthesis, is preferably a hydrogen atom or an alkyl group having a carbon number of 1 to 12, more preferably a hydrogen atom or a methyl group, still more preferably a methyl group.

In formulae (3) and (4), R' represents a branched or linear alkylene group (the carbon number is preferably from 1 to 10, more preferably 2 or 3) and is preferably a group represented by $-\text{CH}_2-\text{CH}(\text{CH}_3)-$ in formula (3) and a group represented by $-\text{CH}(\text{CH}_3)-\text{CH}_2-$ in formula (4).

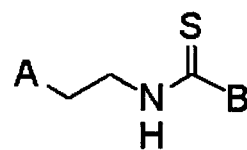
In formulae (1) to (5), each of Y^1 , Y^2 , Y^3 , Y^4 and Y^5 independently represents a divalent linking group and is not particularly restricted in view of structure. Specific examples thereof include the following linking groups (Y-1) to (Y-20). In the structures below, A and B indicate bonds to the left terminal group and the right terminal group, respectively, in formulae (1) to (5). Among the structures shown below, in view of easy synthesis, (Y-2) and (Y-13) are preferred.



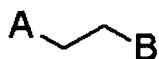
(Y-1)



(Y-2)



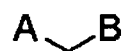
(Y-3)



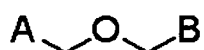
(Y-4)



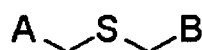
(Y-5)



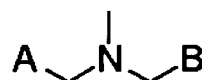
(Y-6)



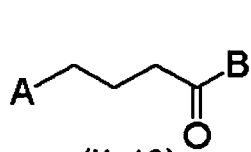
(Y-7)



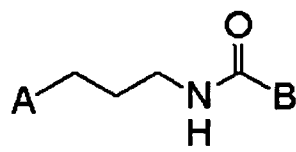
(Y-8)



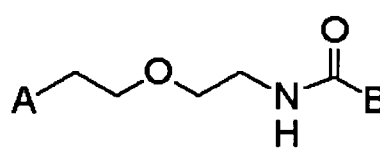
(Y-9)



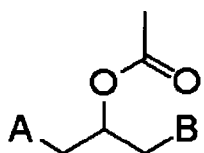
(Y-10)



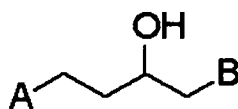
(Y-11)



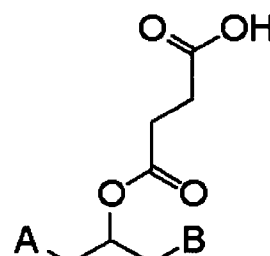
(Y-12)



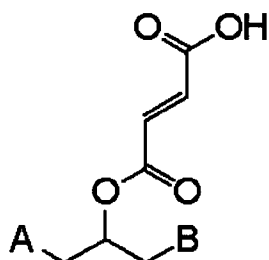
(Y-13)



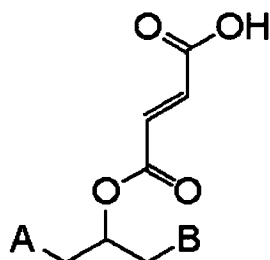
(Y-14)



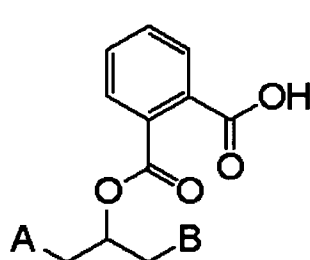
(Y-15)



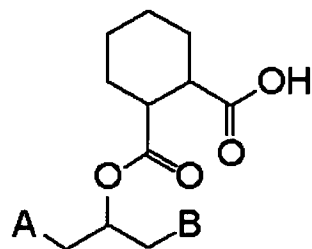
(Y-16)



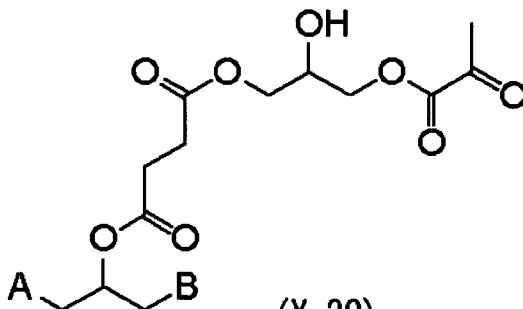
(Y-17)



(Y-18)



(Y-19)



(Y-20)

In formulae (1) to (5), each of Z^1 , Z^2 , Z^3 , Z^4 and Z^5 independently represents a hydrogen atom or a monovalent substituent, and the structure of the substituent is not particularly limited. Specific examples thereof include an alkyl group, a hydroxyl group, an alkoxy group, an aryloxy group, a heteroaryloxy group, an alkylthioether group, an arylthioether group, a heteroarylthioether group and an amino group. Among these, from the standpoint of enhancing the dispersibility, those having a steric repulsion effect are preferred, and an alkyl group having a carbon number of 5 to 24 is preferred. Above all, a branched alkyl group having a carbon number of 5 to 24 or a cyclic alkyl group having a carbon number of 5 to 24 is preferred.

In formulae (1) to (5), each of n , m , p , q and r represents an integer of 1 to 500.

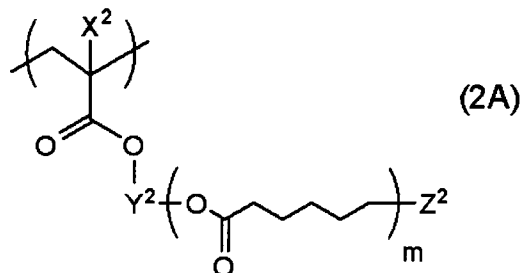
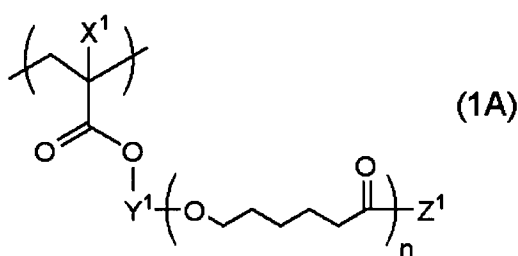
In formulae (1) and (2), each of j and k independently represents an integer of 2 to 8. In view of dispersion stability and developability, each of j and k in formulae (1) and (2) is preferably an integer of 4 to 6, and most preferably 5.

In formula (5), R represents a hydrogen atom or a monovalent organic group and is not particularly limited in its structure but is preferably a hydrogen atom, an alkyl group, an aryl group or a heteroaryl group, more preferably a hydrogen atom or an alkyl group. When R is an alkyl group, the alkyl group is preferably a linear alkyl group having a carbon number of 1 to 20, a branched alkyl group having a carbon number of 3 to 20, or a cyclic alkyl group having a carbon number of 5 to 20, more preferably a linear alkyl group having a carbon number of 1 to 20, still more preferably a linear alkyl group having a carbon number of 1 to 6.

As for R in formula (5), two or more R 's differing in the structure may be mixed and used in the specific resin.

In view of dispersion stability and developability, the structural unit represented by formula (1) is preferably a structural unit represented by the following formula (1A).

Also, in view of dispersion stability and developability, the structural unit represented by formula (2) is preferably a structural unit represented by the following formula (2A).



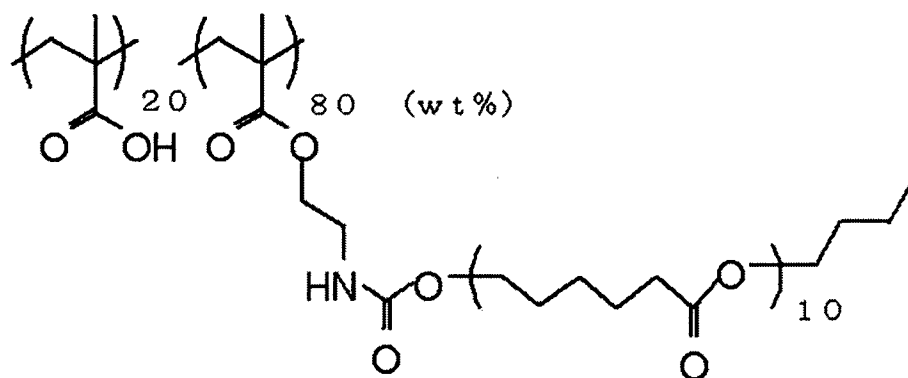
In formula (1A), X^1 , Y^1 , Z^1 and n have the same meanings as X^1 , Y^1 , Z^1 and n in formula (1), and preferred ranges are also the same.

In formula (2A), X^2 , Y^2 , Z^2 and m have the same meanings as X^2 , Y^2 , Z^2 and m in formula (2), and preferred ranges are also the same.

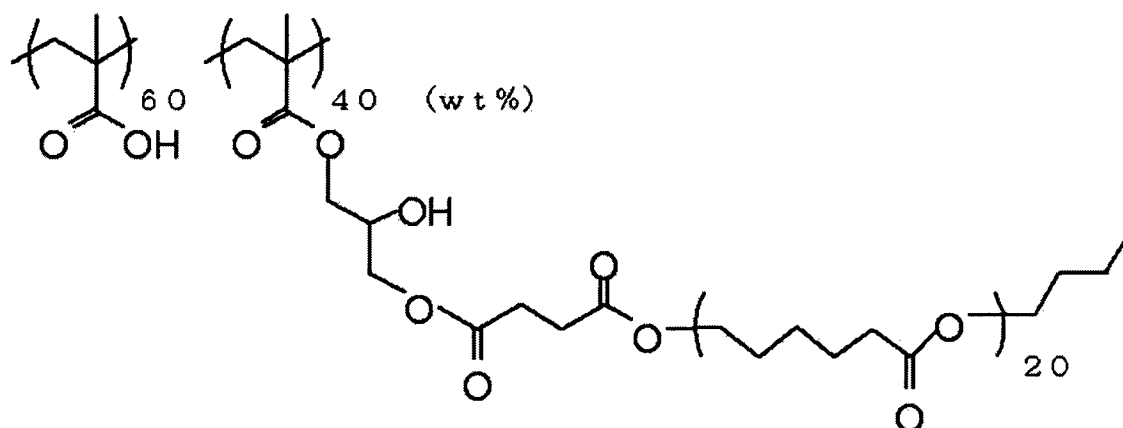
Above all, a compound having a polyester chain in the side chain, represented by formula (1), is preferred. As representative compounds thereof, Exemplified Compounds 1 to 71 described in paragraphs [0046] to [0078] of JP-A-2010-106268 can be suitably used as the dispersant also in the present invention.

Exemplified Compounds 1 to 50 are illustrated below as the dispersant suitable for the present invention, but the present invention is not limited thereto. In the compounds illustrated below, the numerical value attached to each structural unit (the numerical value attached to the repeating unit of the main chain) indicates the content [% by mass; shown as "wt%"] of the structural unit. The numerical value attached to the repeating unit of the side chain indicates the number of repetitions of the repeating unit.

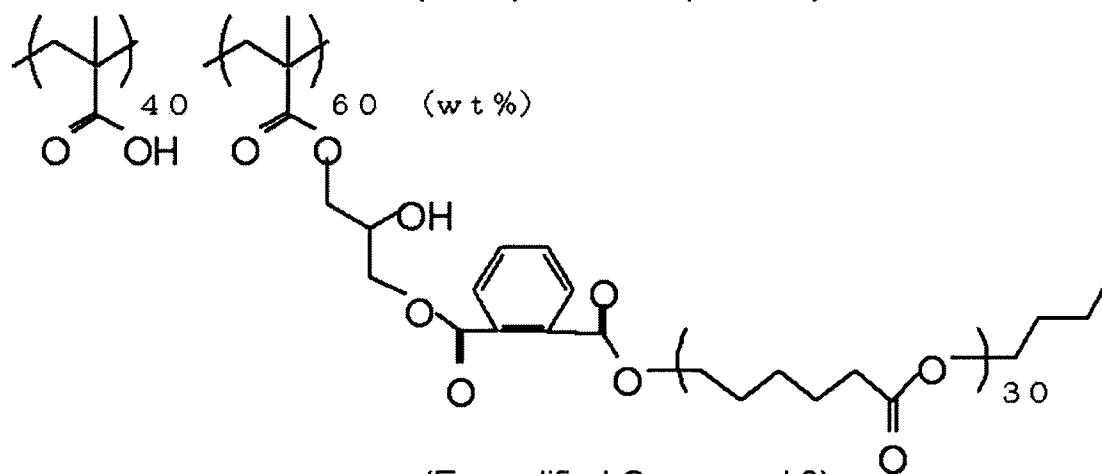
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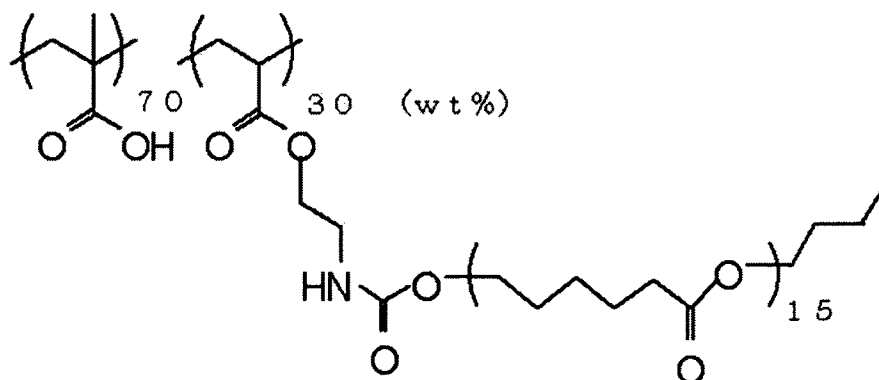
(Exemplified Compound 1)



(Exemplified Compound 2)

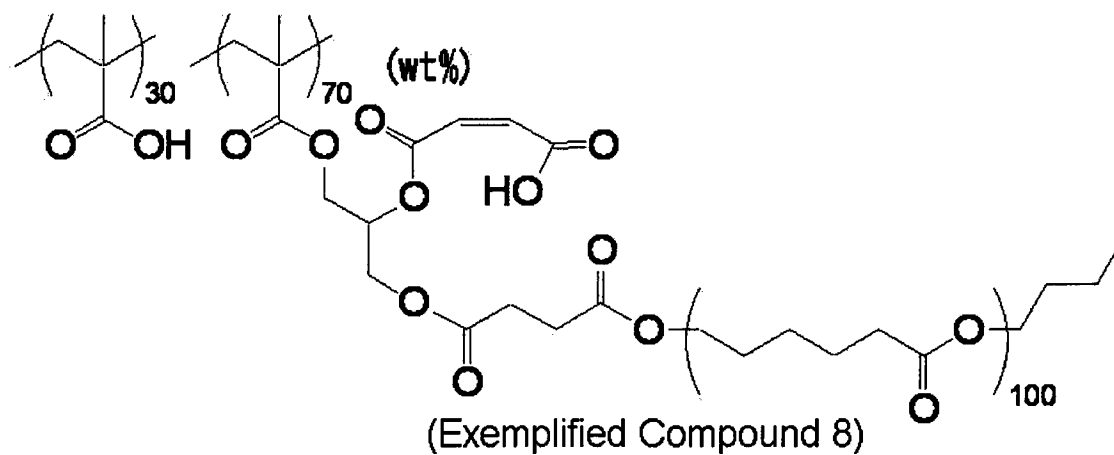
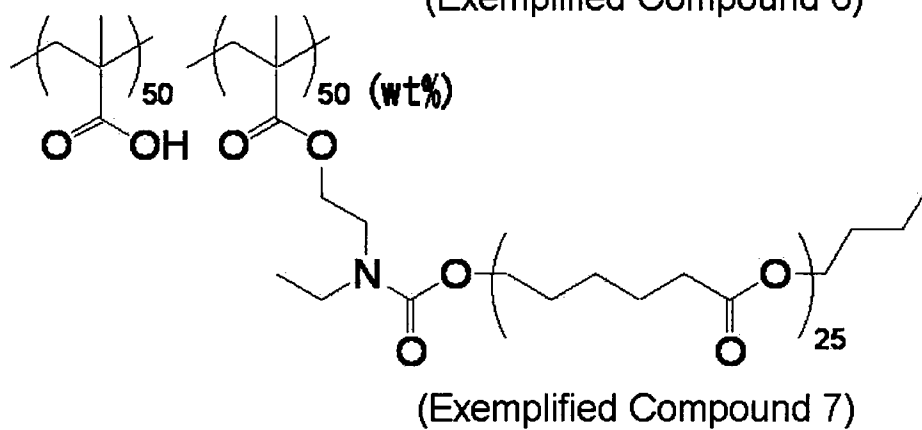
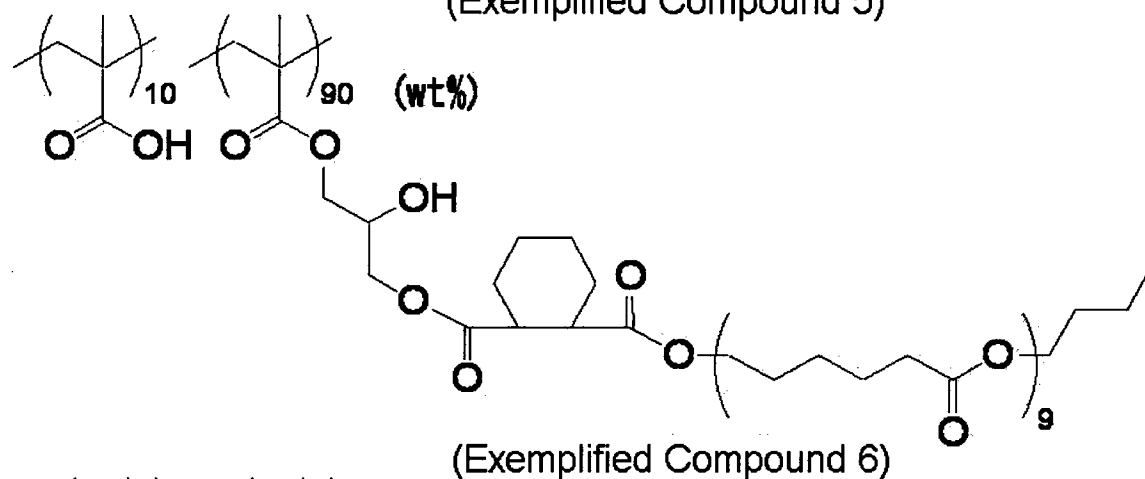
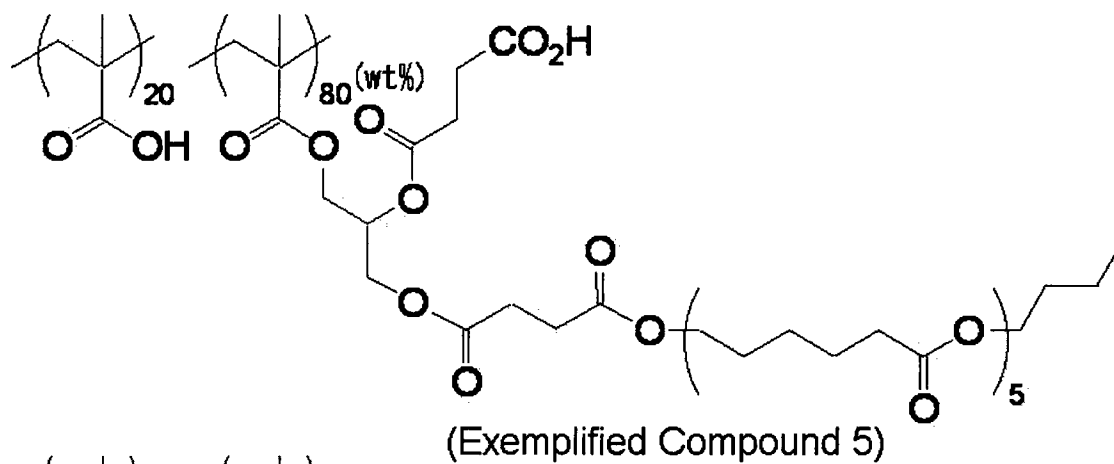


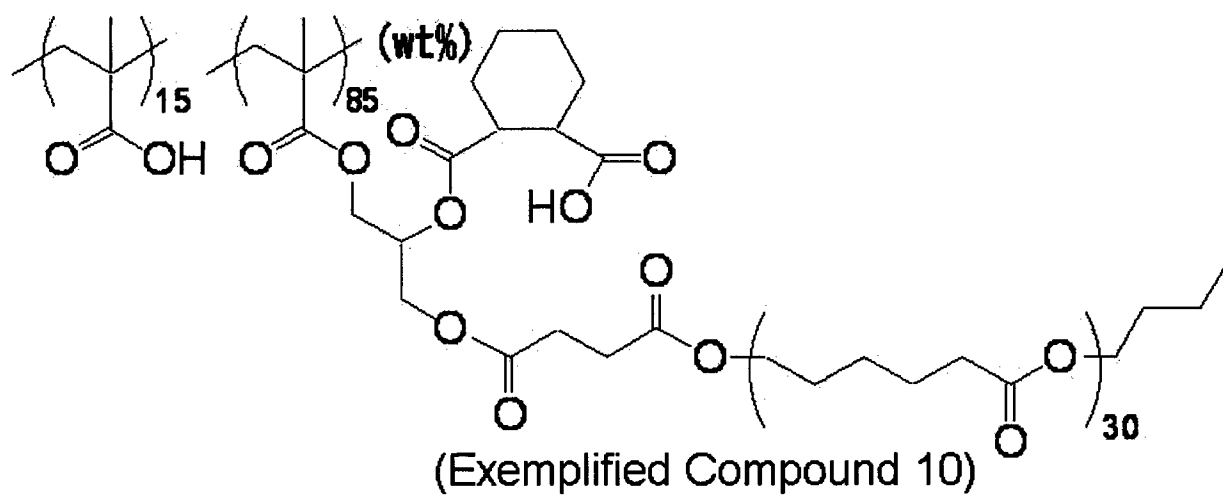
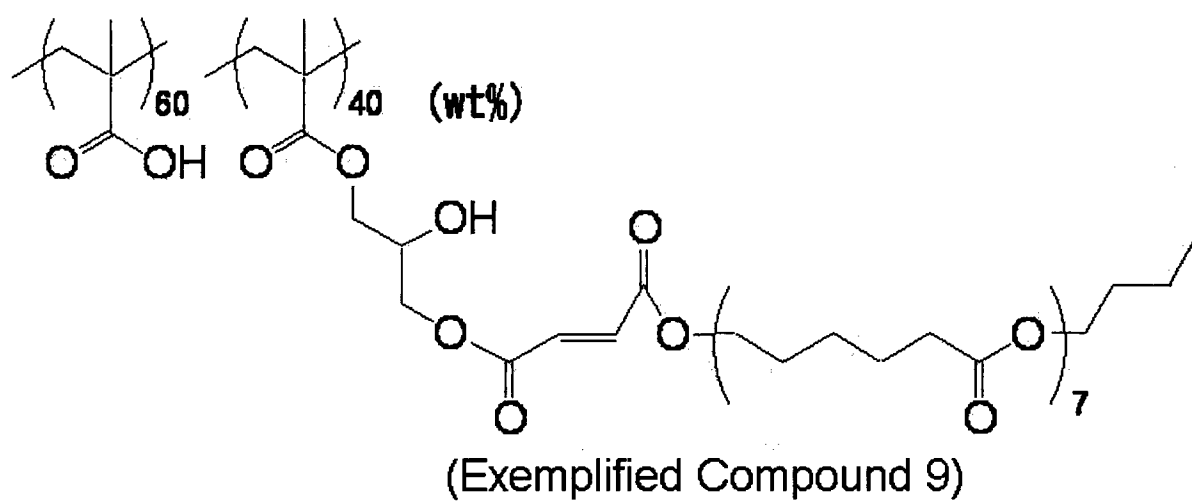
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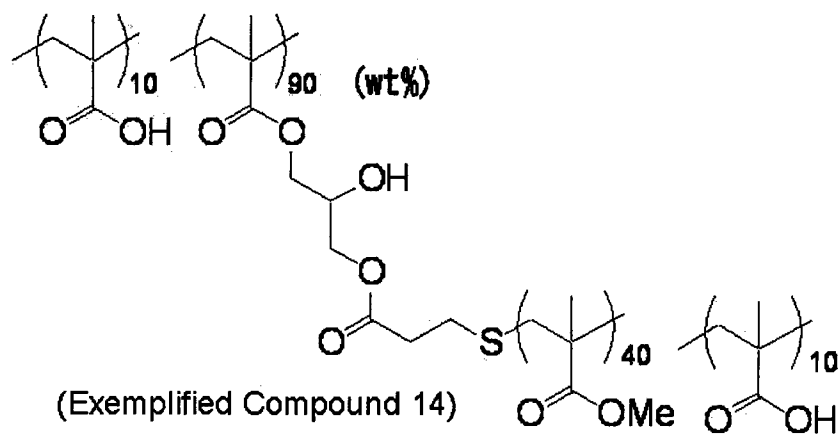
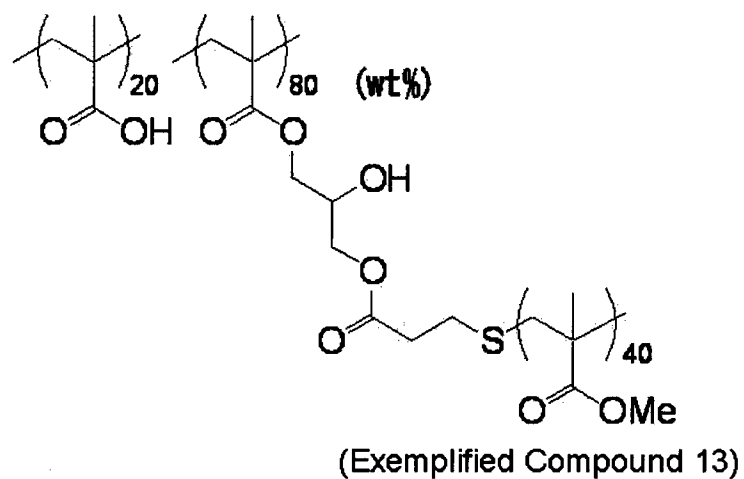
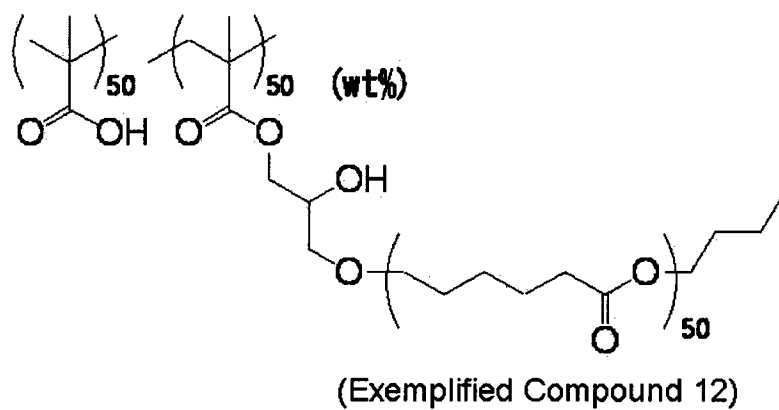
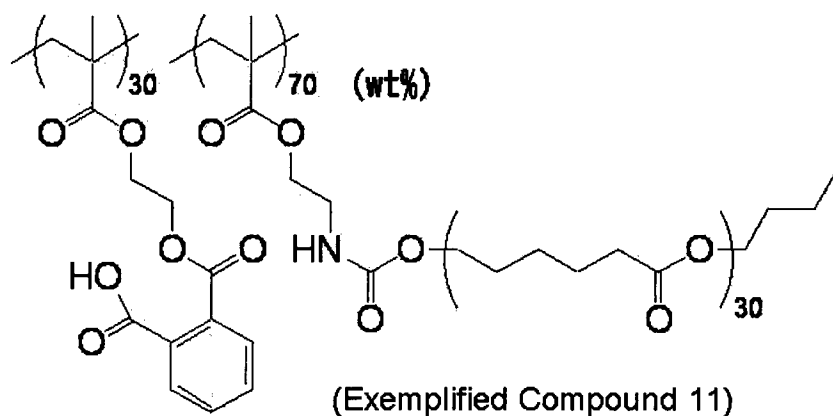


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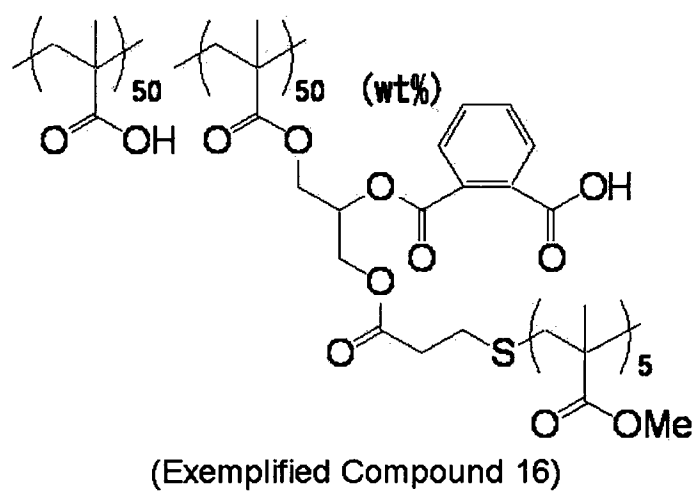
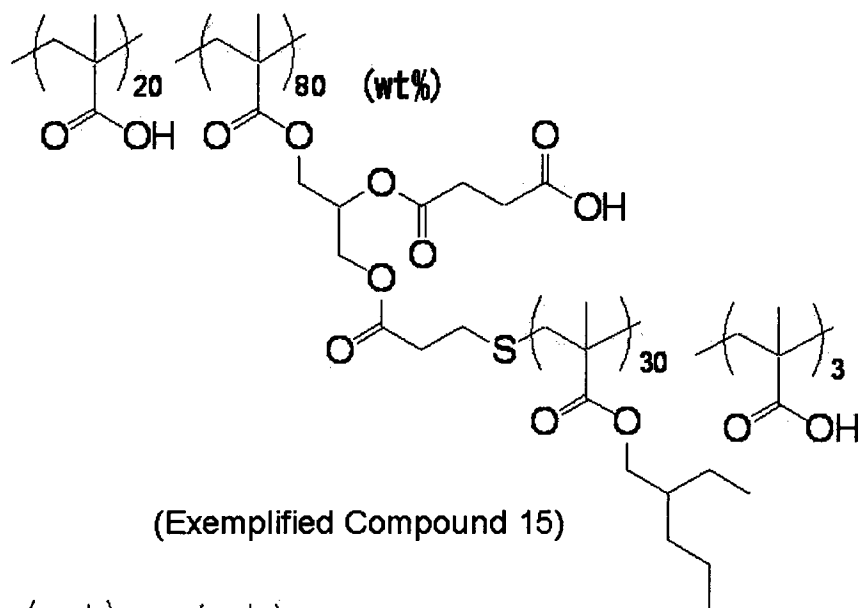
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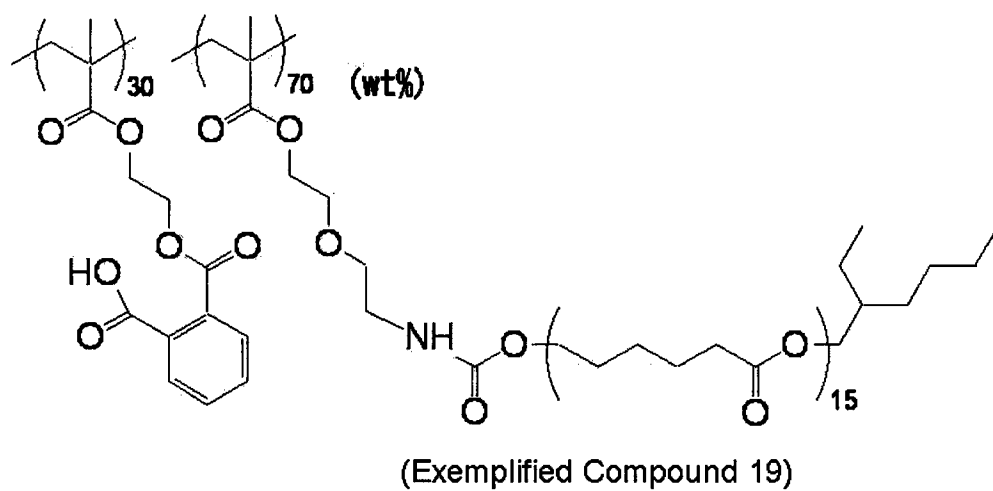
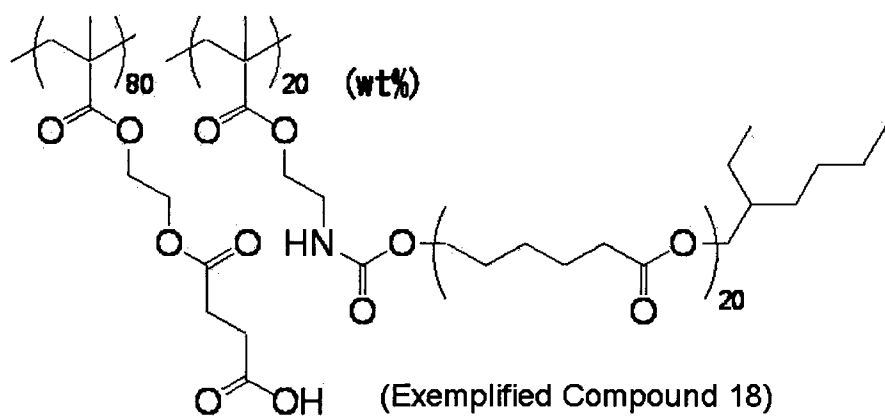
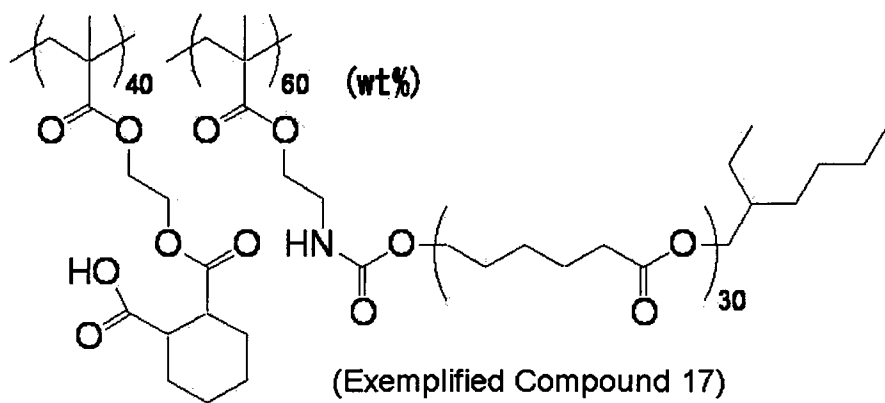


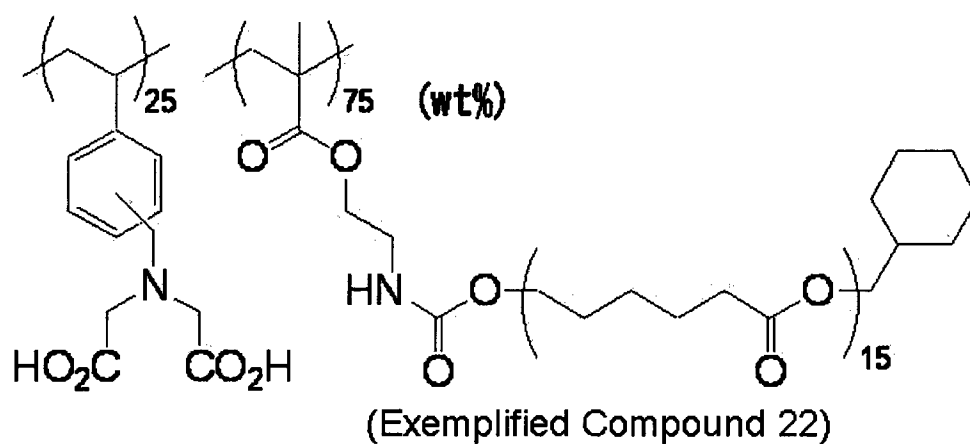
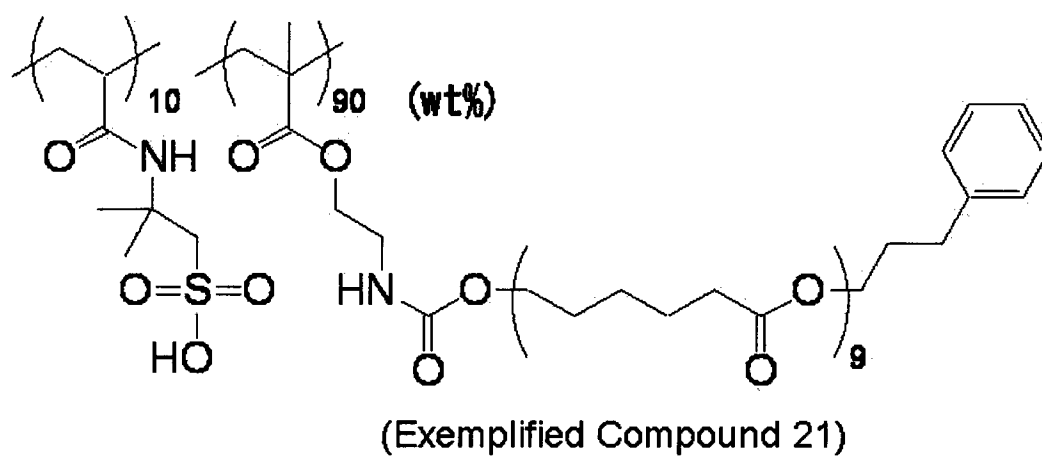
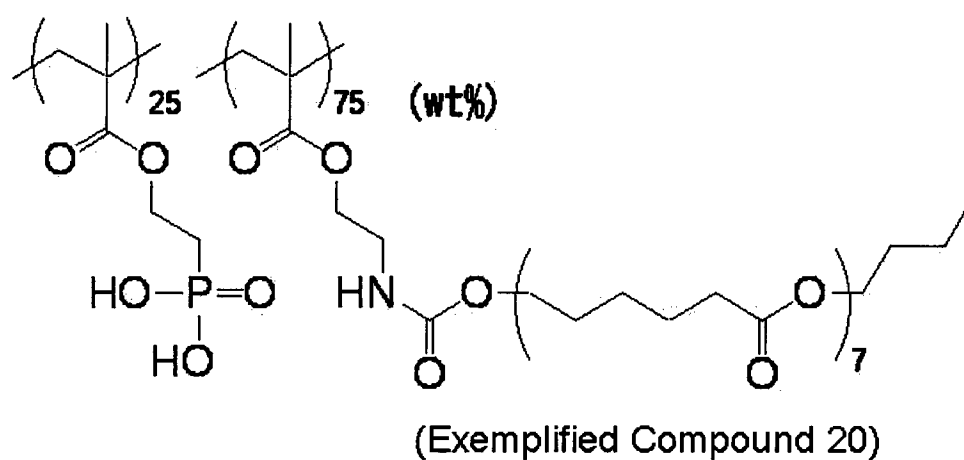


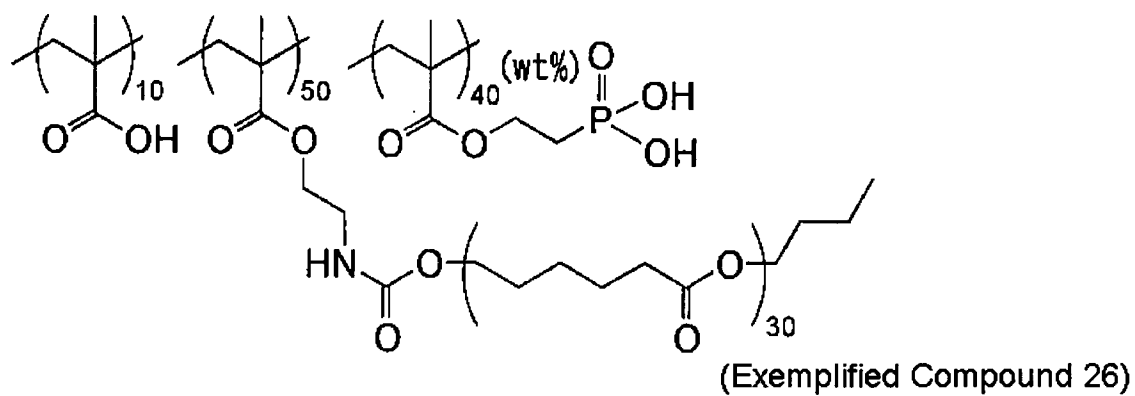
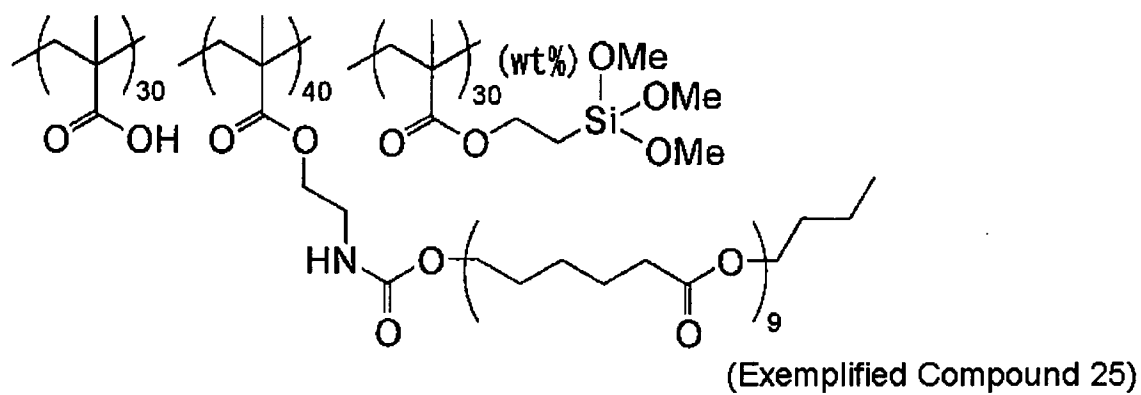
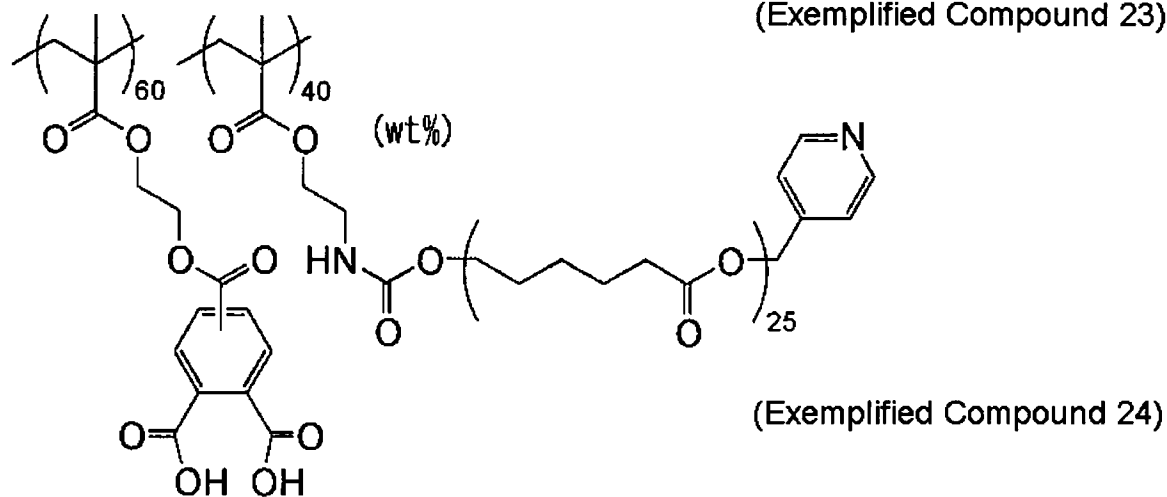
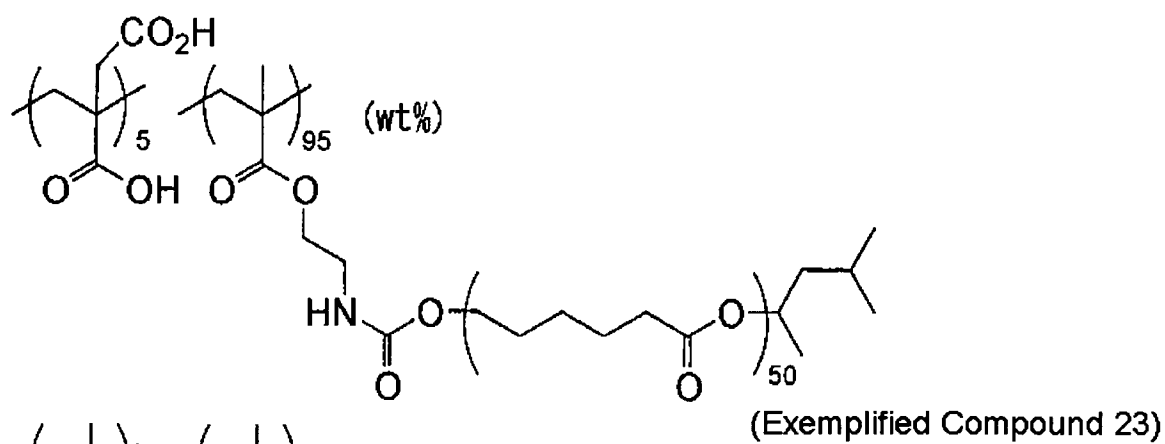
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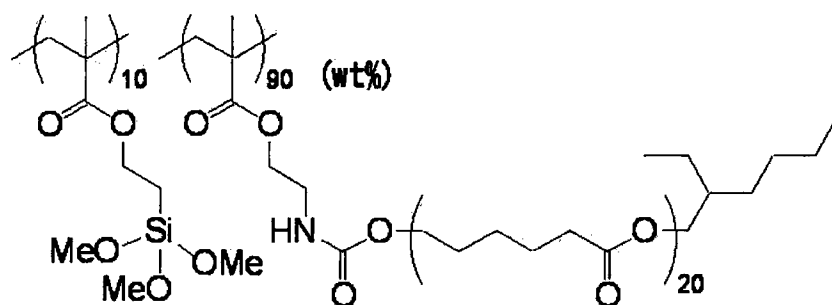


(Exemplified)

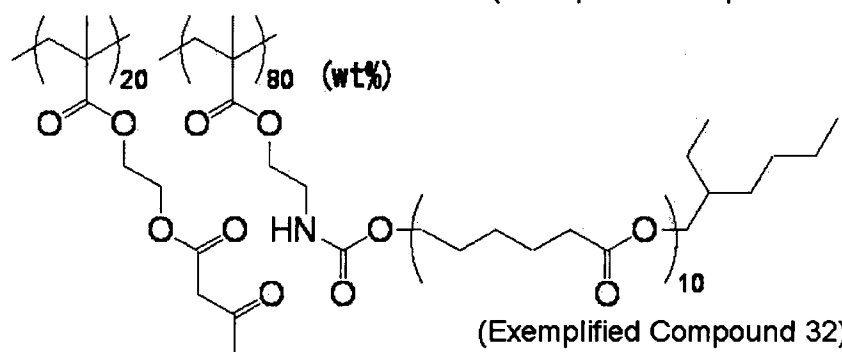
Chemical structure of a copolymer (Exemplified) showing two repeating units. The first unit is a poly(amide) with a p-phenylene group and a hydroxyl group, labeled 60 (wt%). The second unit is a poly(amide) with a p-phenylene group and a hydroxyl group, labeled 40 (wt%). The side chain of the second unit contains a hexamethylene group and a hydroxyl group, connected via an ester linkage.

CC(C)(C)OC(=O)OCCNCCOC(=O)C()C(C)C
 40 (wt%) 60
 80

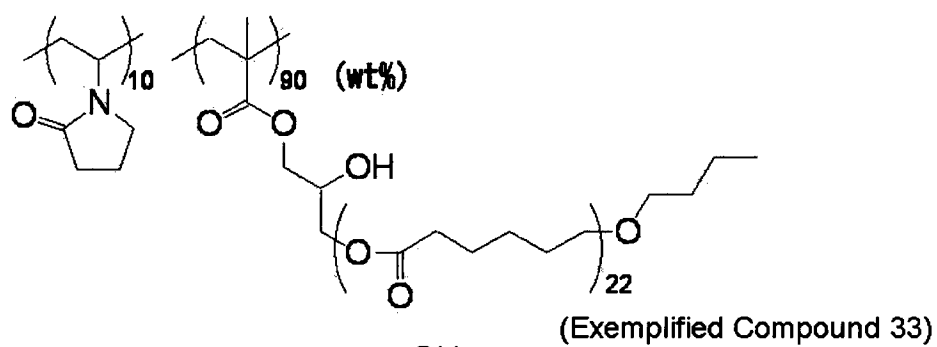
47



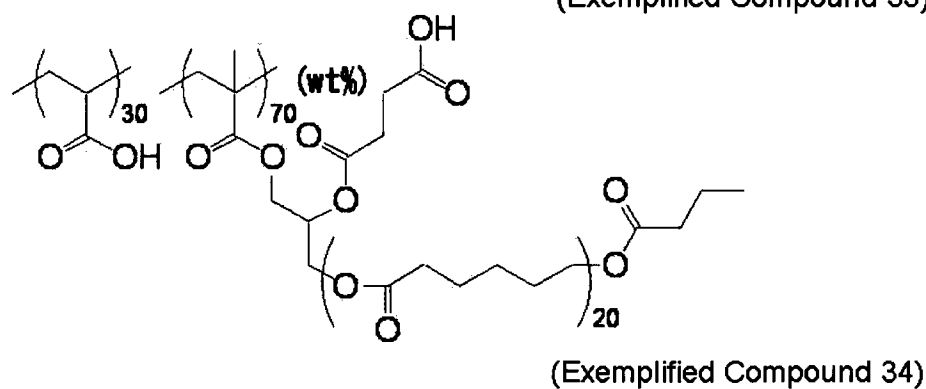
(Exemplified Compound 31)



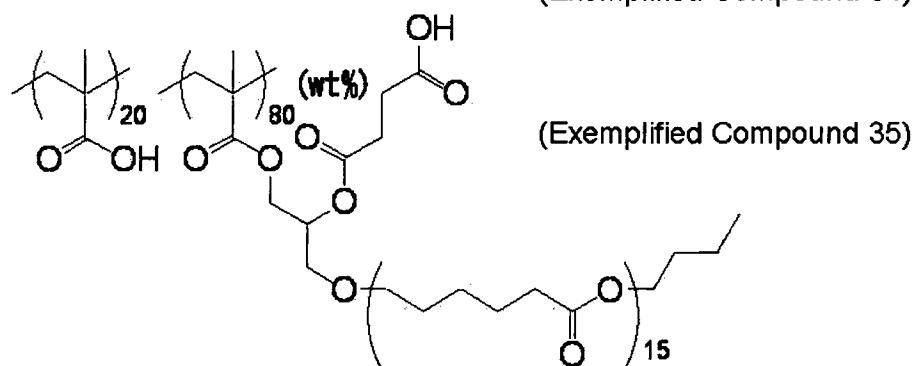
(Exemplified Compound 32)



(Exemplified Compound 33)

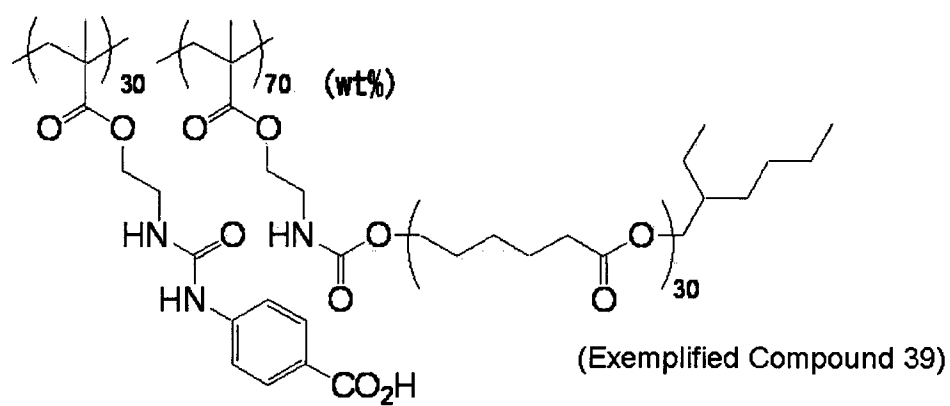
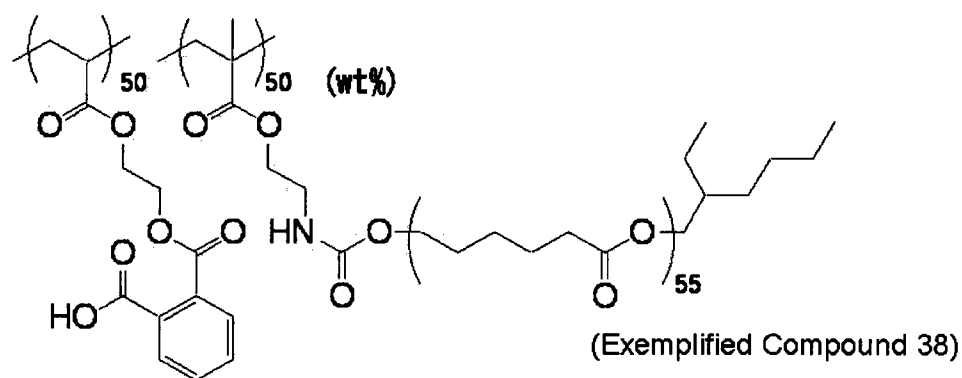
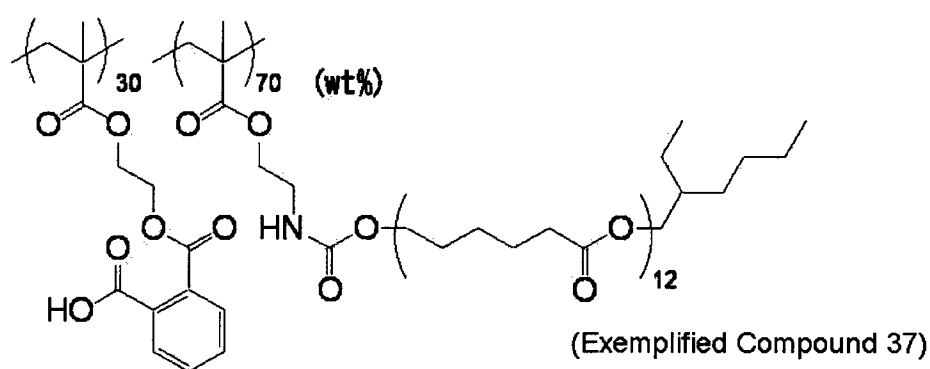
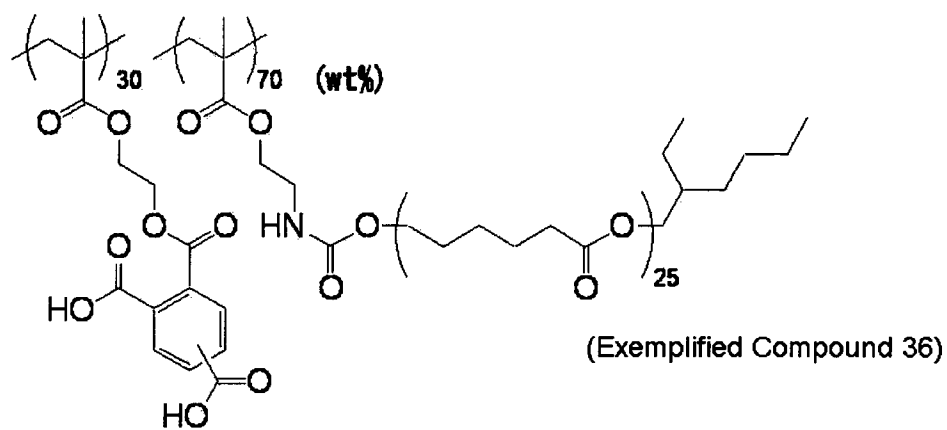


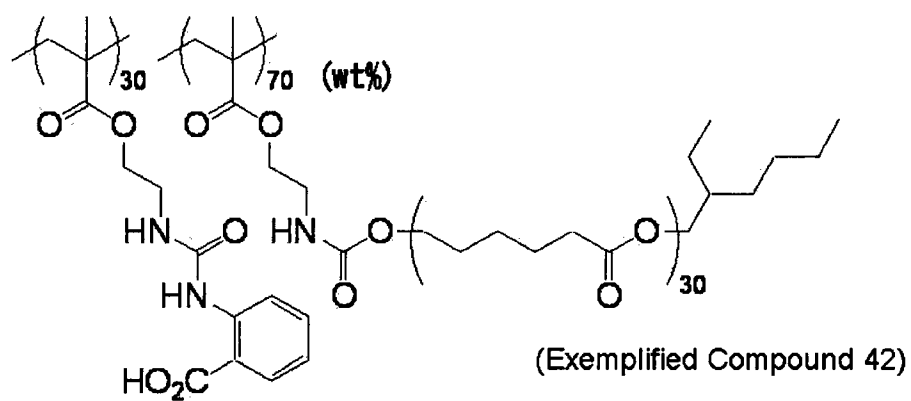
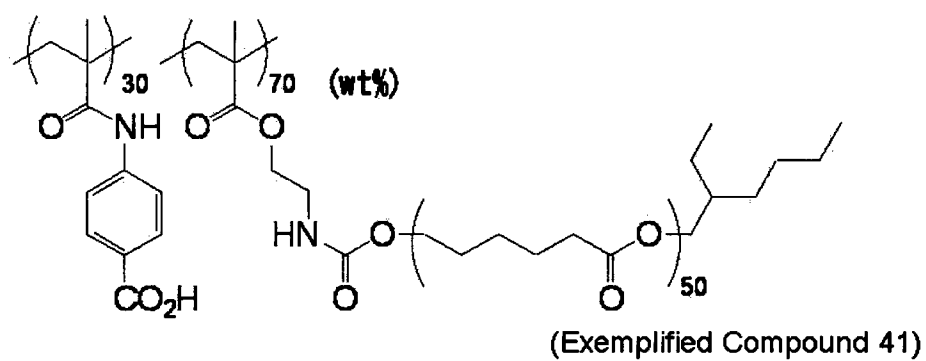
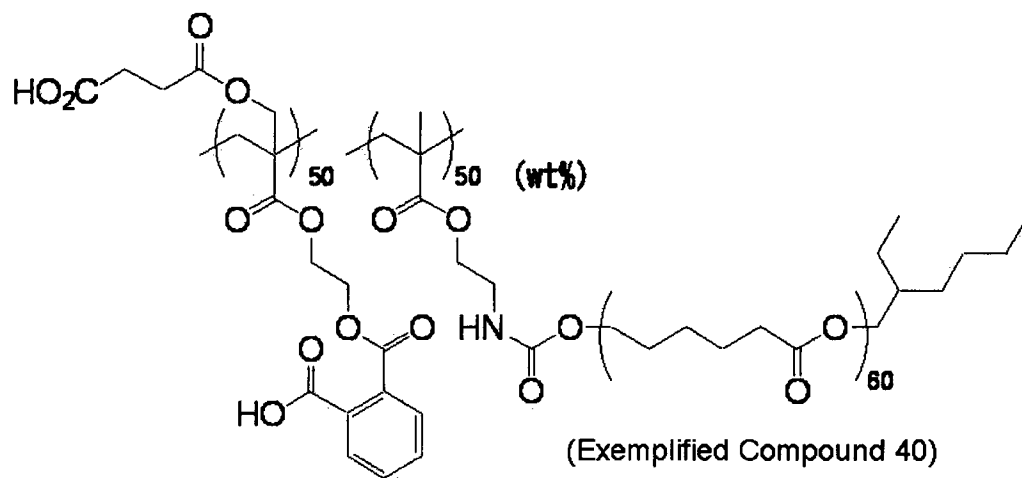
(Exemplified Compound 34)



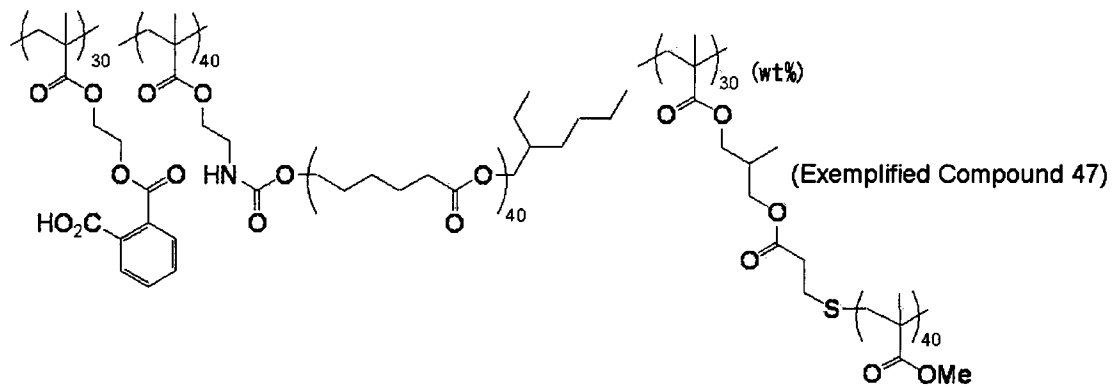
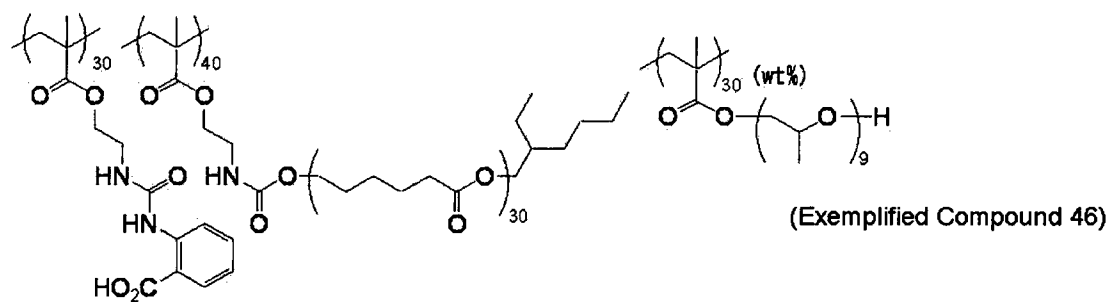
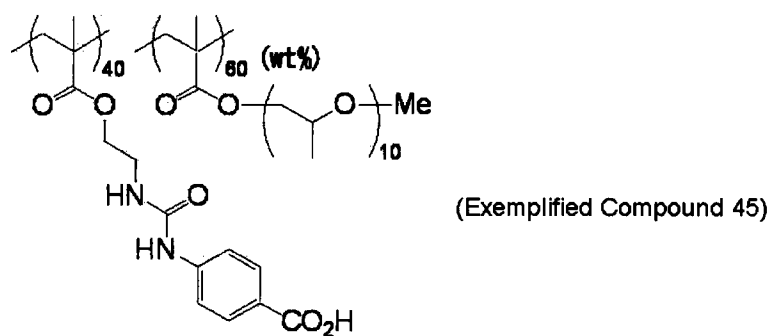
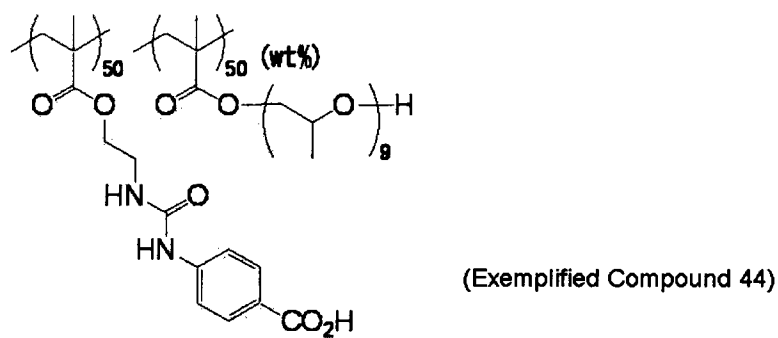
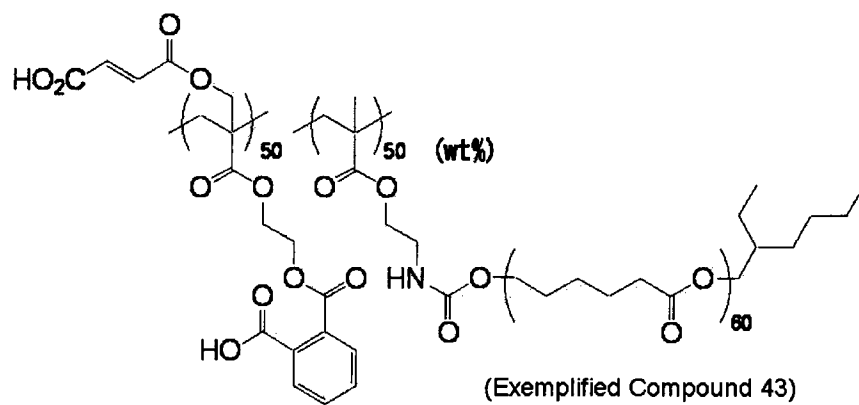
(Exemplified Compound 35)

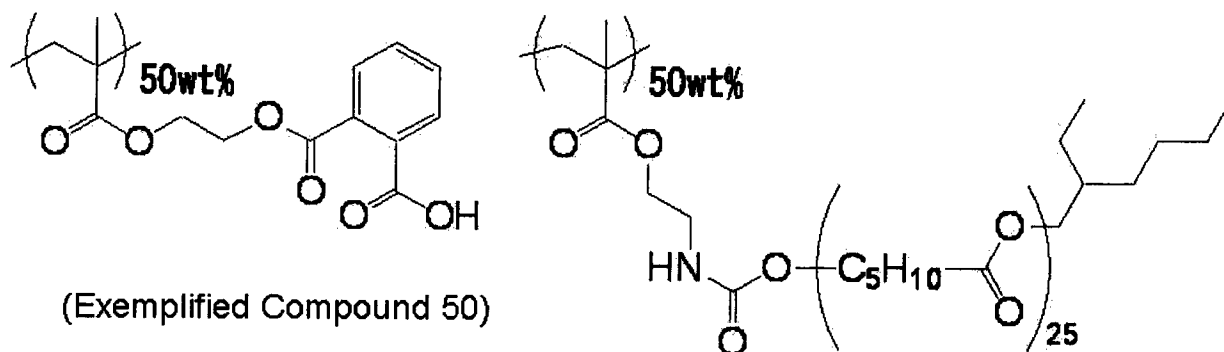
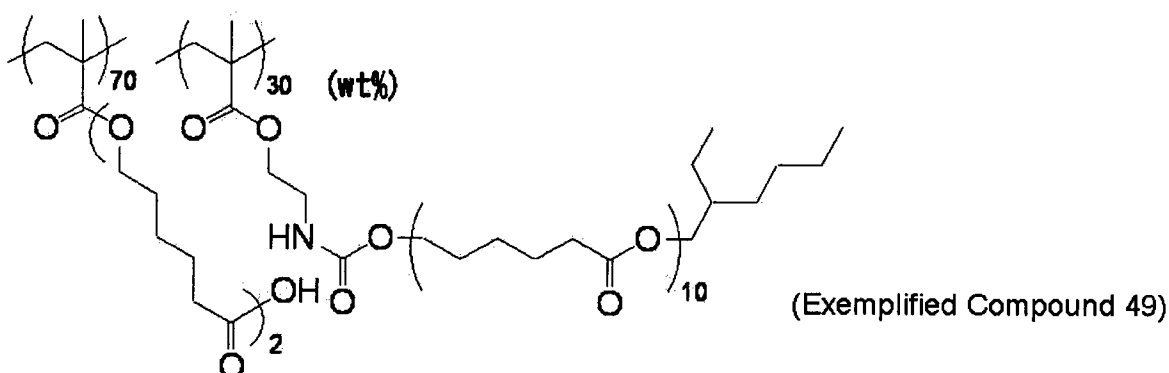
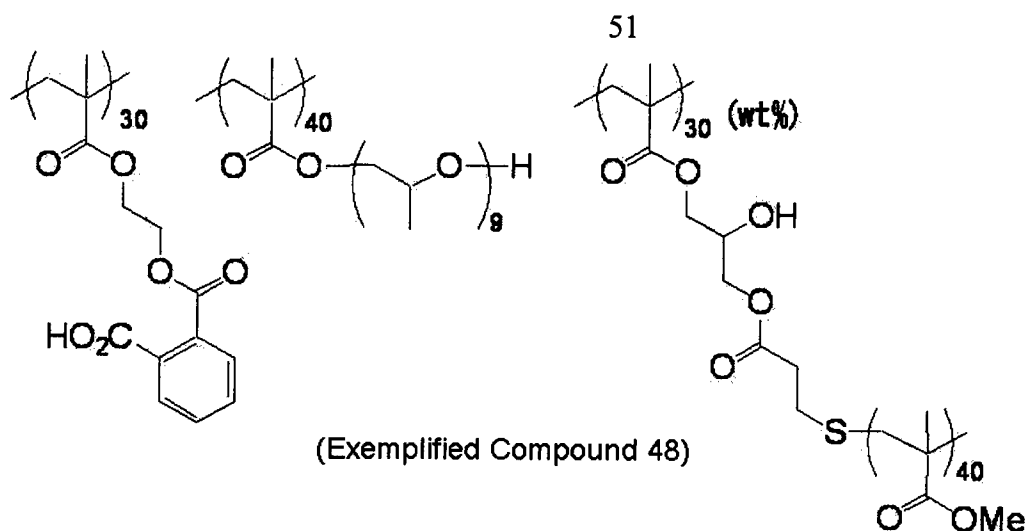
48





50





In view of dispersibility, developability and precipitation property, the dispersant is preferably a resin having a polyester chain in the side chain, and in view of dispersibility and resolution property, a resin further having an acid group is preferred. The acid group is, in view of adsorptive property, preferably an acid group having pKa of 6 or less, more preferably an acid group derived from a carboxylic acid, a sulfonic acid or a phosphoric acid.

In view of solubility in the dispersion solution as well as dispersibility and developability, a resin having a carboxylic acid group, where the polyester chain is a polycaprolactone side chain, is most preferred.

An amphoteric dispersant such as Hinoact T-8000E produced by Kawaken Fine

Chemicals, Ltd. may be also used as the dispersant.

In the case of using a dispersant, from the standpoint of enhancing the dispersibility, a dispersion composition is preferably prepared using the tungsten compound (and the other infrared-blocking material, if desired), a dispersant and an appropriate solvent and then blended in the polymerizable composition.

The polymerizable composition may or may not contain a dispersant, but in the case of containing a dispersant, the content thereof in the dispersion composition is preferably from 1 to 90 mass%, more preferably from 3 to 70 mass%, based on the entire solid content by mass of the tungsten compound in the dispersion composition or in the case of using the other infrared-blocking material and using an infrared-absorbent inorganic pigment as the other infrared-blocking material, based on the sum of the entire solid contents by mass of the tungsten compound and the infrared-absorbent inorganic pigment.

[8] Sensitizer

The polymerizable composition of the present invention preferably contains a sensitizer for the purpose of enhancing the radical generating efficiency of the polymerization initiator and shifting the photosensitive wavelength to the longer wavelength side. The sensitizer which can be used in the present invention is preferably a sensitizer capable of sensitizing the photopolymerization initiator by an electron transfer mechanism or an energy transfer mechanism. The sensitizer which can be used in the present invention includes those belonging to the compounds enumerated below and having an absorption wavelength in the wavelength region of 300 to 450 nm.

Preferred examples of the sensitizer include those belonging to the following compounds and having an absorption wavelength in the wavelength region of 330 to 450 nm.

Examples include a polynuclear aromatic compound (e.g., phenanthrene, anthracene, pyrene, perylene, triphenylene, 9,10-dialkoxanthracene), a xanthene-based compound (e.g., fluorescein, eosin, erythrosine, Rhodamine B, Rose Bengal), a thioxanthone-based compound (e.g., isopropylthioxanthone, diethylthioxanthone, chlorothioxanthone), an acridone-based compound (e.g., acridone, chloroacridone, N-methylacridone, N-butylacridone, 10-n-butyl-2-chloroacridone), a cyanine-based compound (e.g., thiocarbocyanine, oxacarbocyanine), a merocyanine-based compound (e.g., merocyanine, carbomerocyanine), a phthalocyanine-based compound, a thiazine-based compound (e.g., thionine, methylene blue, toluidine blue), an acridine-based compound (e.g., acridine orange, chloroflavin, acriflavin), an anthraquinone-

based compound (e.g., anthraquinone), a squarylium-based compound (e.g., squarylium), acridine orange, a coumarin-based compound (e.g., coumarin, 7-diethylamino-4-methylcoumarin), ketocoumarin, a phenothiazine-based compound, a phenazine-based compound, a styrylbenzene-based compound, an azo compound, diphenylmethane, triphenylmethane, distyrylbenzene-based compound, a carbazole-based compound, porphyrin, a spiro compound, quinacridone, indigo, styryl, a pyrylium compound, a pyromethene compound, a pyrazolotriazole compound, a benzothiazole compound, a barbituric acid derivative, a thiobarbituric acid derivative, an aromatic ketone compound such as acetophenone, benzophenone, thioxanthone and Michler's ketone, and a heterocyclic compound such as N-aryl oxazolidinone.

Examples further include compounds described in European Patent 568,993, U.S. Patents 4,508,811 and 5,227,227, JP-A-2001-125255 and JP-A-11-271969.

Above all, the sensitizer is preferably at least one member selected from a thioxanthone-based compound, an acridone-based compound and a coumarin-based compound, and a thioxanthone-based compound is more preferred. By combining such a sensitizer with the above-described polymerization initiator, high sensitivity can be more reliably obtained.

The polymerizable composition may or may not contain the sensitizer but in the case of containing the sensitizer, the content thereof is preferably from 0.01 to 10 mass%, more preferably from 0.1 to 2 mass%, based on the entire solid content by mass of the polymerizable composition of the present invention.

[9] Crosslinking agent

The polymerizable composition of the present invention may further contain a crosslinking agent for the purpose of enhancing the strength of the permanent pattern.

The crosslinking agent is not particularly limited as long as it is a compound having a crosslinking group, and the compound preferably has two or more crosslinking groups. Specific preferred examples of the crosslinking group include an oxetane group, a cyanate group, and the same groups as those described for the crosslinking group which the alkali-soluble binder may have. Among these, an epoxy group, an oxetane group and a cyanate group are preferred. That is, the crosslinking group is preferably an epoxy compound, an oxetane compound or a cyanate compound.

Examples of the epoxy compound which can be suitably used as the crosslinking agent in the present invention include an epoxy compound containing at least two oxirane

groups per molecule, and an epoxy compound containing, per molecule, at least two epoxy groups each having an alkyl group at the β -position.

Examples of the epoxy compound having at least two oxirane groups per molecule include, but are not limited to, a bixylenol-type or biphenol-type epoxy compound (e.g., "YX4000 produced by Japan Epoxy Resins Co., Ltd."), a mixture thereof, a heterocyclic epoxy compound having an isocyanurate framework or the like (e.g., "TEPIC produced by Nissan Chemicals Industries, Ltd.", "ARALDITE PT810 produced by BASF Japan"), a bisphenol A-type epoxy compound, a novolak-type epoxy compound, a bisphenol F-type epoxy compound, a hydrogenated bisphenol A-type epoxy compound, a bisphenol S-type epoxy compound, a phenol novolak-type epoxy compound, a cresol novolak-type epoxy compound, a halogenated epoxy compound (such as low brominated epoxy compound, high halogenated epoxy compound, brominated phenol novolak-type epoxy compound), an allyl group-containing bisphenol A-type epoxy compound, a trisphenolmethane-type epoxy compound, a diphenyldimethanol-type epoxy compound, a phenol biphenylene-type epoxy compound, a dicyclopentadiene-type epoxy compound (e.g., "HP-7200, HP-7200H produced by Dainippon Ink and Chemicals, Inc."), a glycidylamine-type epoxy compound (such as diaminodiphenylmethane-type epoxy compound, glycidylaniline and triglycidylaminophenol), a glycidyl ester-type epoxy compound (e.g., diglycidyl phthalate, diglycidyl adipate, diglycidyl hexahydrophthalate, diglycidyl dimerate), a hydantoin-type epoxy compound, an alicyclic epoxy compound (e.g., 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate, bis(3,4-epoxycyclohexylmethyl)adipate, dicyclopentadiene diepoxide, "GT-300, GT-400, ZEHPE3150 produced by Daicel Chemical Industries, Ltd."), an imide-type alicyclic epoxy compound, a trihydroxyphenylmethane-type epoxy compound, bisphenol A novolak-type epoxy compound, a tetraphenylene-type epoxy compound, a glycidyl phthalate compound, a tetraglycidyl xylenoylethane compound, a naphthalene group-containing epoxy compound (such as naphthol aralkyl-type epoxy compound, naphthol novolak-type epoxy compound, tetrafunctional naphthalene-type epoxy compound, and commercially available "ESN-190, ESN-360 produced by Nippon Steel Chemical Co., Ltd.", and "HP-4032, EXA-4750, EXA-4700 produced by Dainippon Ink and Chemicals, Inc."), a reaction product of epichlorohydrin with a polyphenol compound obtained by an addition reaction between a phenol compound and a diolefin compound such as divinylbenzene and dicyclopentadiene, a 4-vinylcyclohexene-1-oxide ring-opening polymerization product epoxidized with peracetic

acid or the like, an epoxy compound having a linear phosphorus-containing structure, an epoxy compound having a cyclic phosphorus-containing structure, an α -methylstilbene-type liquid crystal epoxy compound, a dibenzoyloxybenzene-type liquid crystal epoxy compound, an azophenyl-type liquid crystal epoxy compound, an azomethine phenyl-type liquid crystal epoxy compound, a binaphthyl-type liquid crystal epoxy compound, an azine-type epoxy compound, a glycidyl methacrylate copolymer-based epoxy compound (e.g., "CP-50S, CP-50M produced by NOF Corporation"), a copolymerized epoxy compound of cyclohexyl maleimide and glycidyl methacrylate, a bis(glycidylloxyphenyl)fluorene-type epoxy compound, and a bis(glycidylloxyphenyl)adamantane-type epoxy compound. One of these epoxy resins may be used alone, or two or more thereof may be used in combination.

Moreover, other than the epoxy compound containing at least two oxirane groups per molecule, an epoxy compound containing, per molecule, at least two epoxy groups each having an alkyl group at the β -position may be used, and a compound containing an epoxy group substituted with an alkyl group at the β -position (more specifically, a β -alkyl-substituted glycidyl group or the like) is particularly preferred.

In the epoxy compound containing at least an epoxy group having an alkyl group at the β -position, all of two or more epoxy groups contained per molecule may be a β -alkyl-substituted glycidyl group, or at least one epoxy group may be a β -alkyl-substituted glycidyl group.

Examples of the oxetane compound include an oxetane resin having at least two oxetanyl groups per molecule.

Specific examples thereof include polyfunctional oxetanes such as bis[(3-methyl-3-oxetanylmethoxy)methyl]ether, bis[(3-ethyl-3-oxetanylmethoxy)methyl]ether, 1,4-bis[(3-methyl-3-oxetanylmethoxy)methyl]benzene, 1,4-bis[(3-ethyl-3-oxetanylmethoxy)methyl]benzene, (3-methyl-3-oxetanyl)methyl acrylate, (3-ethyl-3-oxetanyl)methyl acrylate, (3-methyl-3-oxetanyl)methyl methacrylate, (3-ethyl-3-oxetanyl)methyl methacrylate, and an oligomer or copolymer thereof; and ether compounds of an oxetane group-containing compound and a hydroxyl group-containing resin such as novolak resin, poly(p-hydroxystyrene), cardo-type bisphenols, calixarenes, calixresorcinarenes and silsesquioxane. Other examples include a copolymer of an oxetane ring-containing unsaturated monomer and an alkyl (meth)acrylate.

Examples of the bismaleimide compound include 4,4'-diphenylmethane bismaleimide, bis-(3-ethyl-5-methyl-4-maleimidophenyl)methane, and 2,2'-bis-[4-(4-

maleimidophenoxy)phenyl]propane.

Examples of the cyanate compound include a bis A-type cyanate compound, a bis F-type cyanate compound, a cresol novolak-type cyanate compound, and a phenol novolak-type cyanate compound.

The polymerizable composition may or may not contain a crosslinking agent, but in the case of containing a crosslinking agent, the content thereof is preferably from 1 to 40 mass%, more preferably from 3 to 20 mass%, based on the entire solid content by mass of the polymerizable composition of the present invention.

[10] Curing accelerator

The polymerizable composition of the present invention may further contain a curing accelerator for the purpose of accelerating thermal curing of the crosslinking agent such as the above-described epoxy compound and oxetane compound.

Examples of the curing accelerator which can be used include an amine compound (such as dicyandiamide, benzyldimethylamine, 4-(dimethylamino)-N,N-dimethylbenzylamine, 4-methoxy-N,N-dimethylbenzylamine and 4-methyl-N,N-dimethylbenzylamine), a quaternary ammonium salt compound (such as triethylbenzyl ammonium chloride), a block isocyanate compound (such as dimethylamine), an imidazole derivative-bicyclic amidine compound and a salt thereof (such as imidazole, 2-methylimidazole, 2-ethylimidazole, 2-ethyl-4-methylimidazole, 2-phenylimidazole, 4-phenylimidazole, 1-cyanoethyl-2-phenylimidazole and 1-(2-cyanoethyl)-2-ethyl-4-methylimidazole), a phosphorus compound (such as triphenylphosphine), a guanamine compound (such as melamine, guanamine, acetoguanamine and benzoguanamine), and an S-triazine derivative (such as 2,4-diamino-6-methacryloyloxyethyl-S-triazine, 2-vinyl-2,4-diamino-S-triazine, 2-vinyl-4,6-diamino-S-triazine-isocyanuric acid adduct, 2,4-diamino-6-methacryloyloxyethyl-S-triazine-isocyanuric acid adduct). The curing accelerator is preferably melamine or dicyandiamide. These may be used alone or in combination. One of these compounds may be used alone, or two or more thereof may be used in combination.

The polymerizable composition may or may not contain a curing accelerator, but in the case of containing a curing accelerator, the content thereof is usually from 0.01 to 15 mass%, based on the entire solid content of the polymerizable composition.

[11] Elastomer

The polymerizable composition of the present invention may further contain an elastomer.

By containing an elastomer, the adherence to the conductive layer of a printed wiring board when using the polymerizable composition for a solder resist can be more improved and at the same time, heat resistance, thermal shock resistance, flexibility and toughness of the cured film can be more enhanced.

The elastomer which can be used in the present invention is not particularly limited and may be appropriately selected according to the purpose, and examples thereof include a styrene-based elastomer, an olefin-based elastomer, a urethane-based elastomer, a polyester-based elastomer, a polyamide-based elastomer, an acrylic elastomer, and a silicone-based elastomer. Such an elastomer is composed of a hard segment component and a soft segment component, where in general, the former contributes to heat resistance and strength and the latter contributes to flexibility and toughness. Among these, a polyester-based elastomer is advantageous in view of compatibility with other materials.

Examples of the styrene-based elastomer include a styrene-butadiene-styrene block copolymer, a styrene-isoprene-styrene block copolymer, a styrene-ethylene-butylene-styrene block copolymer, and a styrene-ethylene-propylene-styrene block copolymer. As the component constituting the styrene-based elastomer, other than styrene, a styrene derivative such as α -methylstyrene, 3-methylstyrene, 4-propylstyrene and 4-cyclohexylstyrene can be used. Specific examples thereof include TUFPRENE, SOLPRENE T, ASAPRENE T, Tuftec (all produced by ADEKA), Elastomer AR (produced by Aronkasei Co., Ltd.), Kraton G, Califlex (both produced by Shell in Japan), JSR-TR, TSR-SIS, Dynaron (all produced by JSR), Denka STR (produced by Denki Kagaku Kogyo K.K.), Quintac (produced by ZEON Corporation), TPE-SB Series (produced by Sumitomo Chemical Co., Ltd.), Rabalon (produced by Mitsubishi Chemical Corporation), Septon, HYBRAR (both produced by Kuraray Co., Ltd.), Sumiflex (produced by Sumitomo Bakelite Co., Ltd.), Leostomer, and Actymer (both produced by Riken Vinyl Industry Co., Ltd.).

The olefin-based elastomer is a copolymer of α -olefin having a carbon number of 2 to 20, such as ethylene, propylene, 1-butene, 1-hexene and 4-methyl-pentene, and examples thereof include an ethylene-propylene copolymer (EPR) and an ethylene-propylene-diene copolymer (EPDM). Also, the olefin-based elastomer includes, for example, a copolymer of an α -olefin and a nonconjugated diene having a carbon number of 2 to 20, such as

dicyclopentadiene, 1,4-hexadiene, cyclooctadiene, methylenenorbornene, ethylenenorbornene, butadiene and isoprene, and an epoxidized polybutadiene. The olefin-based elastomer further includes, for example, carboxyl-modified NBR obtained by copolymerizing methacrylic acid with a butadiene-acrylonitrile copolymer. Other examples of the olefin-based elastomer include an ethylene- α -olefin copolymer rubber, an ethylene- α -olefin-nonconjugated diene copolymer rubber, a propylene- α -olefin copolymer rubber, and a butene- α -olefin copolymer rubber.

Specific examples of the olefin-based elastomer include Milastomer (produced by Mitsui Petrochemical Industries, Ltd.), EXACT (produced by Exxon Chemical), ENGAGE (produced by Dow Chemical), hydrogenated styrene-butadiene rubber "DYNABON HSBR" (produced by JSR), butadiene-acrylonitrile copolymer "NBR Series" (produced by JSR), butadiene-acrylonitrile copolymer modified at both ends with a carboxyl group having a crosslinking site "XER Series" (produced by JSR), and epoxidized polybutadiene obtained by partially epoxidizing polybutadiene "BF-1000" (produced by Nippon Soda Co., Ltd.).

The urethane-based elastomer consists of structural units, that is, a hard segment composed of low molecular (short chain) diol and diisocyanate, and a soft segment composed of polymer (long chain) diol and diisocyanate. Examples of the polymer (long chain) diol include polypropylene glycol, polytetramethylene oxide, poly(1,4-butylene adipate), poly(ethylene-1,4-butylene adipate), polycaprolactone, poly(1,6-hexylene carbonate), and poly(1,6-hexylene-neopentylene adipate). The number average molecular weight of the polymer (long chain) diol is preferably from 500 to 10,000. Examples of the low molecular (short chain) diol include ethylene glycol, propylene glycol, 1,4-butanediol, and bisphenol A. The number average molecular weight of the short chain diol has is preferably from 48 to 500. Specific examples of the urethane-based elastomer include PANDEX T-2185 and T-2983N (both produced by DIC Corporation), and Shirakutoran E790.

The polyester-based elastomer is obtained by polycondensing a dicarboxylic acid or a derivative thereof and a diol compound or a derivative thereof. Specific examples of the dicarboxylic acid include an aromatic dicarboxylic acid such as terephthalic acid, isophthalic acid and naphthalenedicarboxylic acid; an aromatic dicarboxylic acid where a hydrogen atom of the above-described aromatic ring is substituted with a methyl group, an ethyl group, a phenyl group or the like; an aliphatic dicarboxylic acids having a carbon number of 2 to 20, such as adipic acid, sebacic acid and dodecanedicarboxylic acid; and an alicyclic dicarboxylic acid such as cyclohexanedicarboxylic acid. One of these compounds or two or more thereof

may be used. Specific examples of the diol compound include an aliphatic or alicyclic diol such as ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,10-decanediol and 1,4-cyclohexanediol, bisphenol A, bis-(4-hydroxyphenyl)-methane, bis-(4-hydroxy-3-methylphenyl)-propane, and resorcin. One of these compounds or two or more thereof may be used. A multi-block copolymer using an aromatic polyester (e.g. polybutylene terephthalate) moiety for the hard segment component and an aliphatic polyester (e.g. polytetramethylene glycol) moiety for the soft segment component, can be used. The polyester-based elastomer includes various grades according to the kind, ratio and difference in the molecular weight of the hard segment and the soft segment. Specific examples of the polyester-based elastomer include Hytrel (produced by Du Pont-Toray Co., Ltd.), PELPRENE (produced by Toyobo Co., Ltd.), and ESPEL (produced by Hitachi Chemical Co., Ltd.).

The polyamide-based elastomer consists of a hard segment composed of polyamide and a soft segment composed of polyether or polyester and is roughly classified into two types, that is, a polyether block amide type and a polyether ester block type. Examples of the polyamide include polyamide-6, polyamide-11, and polyamide-12. Examples of the polyether include polyoxyethylene, polyoxypropylene, and polytetramethylene glycol. Specific examples of the polyamide-based elastomer include UBE Polyamide Elastomer (produced by Ube Industries, Ltd.), DAIAMID (produced by Daicel-Huels), PEBAX (produced by Toray Industries, Inc.), Grilon ELY (EMS Japan), Novamid (produced by Mitsubishi Chemical Corporation), and Grilax (produced by DIC Corporation).

The acrylic elastomer is obtained by copolymerizing an acrylic acid ester such as ethyl acrylate, butyl acrylate, methoxyethyl acrylate and ethoxyethyl acrylate, an epoxy group-containing monomer such as glycidyl methacrylate and alkyl glycidyl ether, and/or a vinyl-based monomer such as acrylonitrile and ethylene. Examples of the acrylic elastomer include an acrylonitrile-butyl acrylate copolymer, an acrylonitrile-butyl acrylate-ethyl acrylate copolymer, and an acrylonitrile-butyl acrylate-glycidyl methacrylate copolymer.

The silicone-based elastomer is mainly composed of an organopolysiloxane and can be classified into a polydimethylsiloxane type, a polymethylphenylsiloxane type and a polydiphenylsiloxane type. An organopolysiloxane partially modified with a vinyl group, an alkoxy group or the like may be also used. Specific examples of the silicone-based elastomer include KE Series (produced by Shin-Etsu Chemical Co., Ltd.), SE Series, CY Series and SH Series (all produced by Dow Corning Toray Silicone Co., Ltd.).

Other than the elastomers described above, a rubber-modified epoxy resin may be

used. The rubber-modified epoxy resin is obtained by modifying a part or all of epoxy groups in the above-described bisphenol F-type epoxy resin, bisphenol A-type epoxy resin, salicylaldehyde-type epoxy resin, phenol novolak-type epoxy resin, cresol novolak-type epoxy resin or the like with, for example, a both-terminal carboxylic acid-modified butadiene-acrylonitrile rubber or a terminal amino-modified silicone rubber.

Among the elastomers, in view of shear adherence and thermal shock resistance, a both-terminal carboxyl group-modified butadiene-acrylonitrile copolymer, and ESPEL that is a polyester-based elastomer having a hydroxyl group (ESPEL 1612 and 1620, produced by Hitachi Chemical Co., Ltd.), and epoxidized polybutadiene are preferred.

The polymerizable composition of the present invention may or may not contain an elastomer, but in the case of containing an elastomer, the content thereof based on the entire solid content by mass of the polymerizable composition is not particularly limited and may be appropriately selected according to the purpose. The content is preferably from 0.5 to 30 mass%, more preferably from 1 to 10 mass%, still more preferably from 3 to 8 mass%, based on the solid content. When the content is in this preferred range, the shear adherence and thermal shock resistance can be advantageously more enhanced.

[12] Surfactant

From the standpoint of more enhancing the coatability, in the photosensitive resin composition of the present invention, various surfactants may be added. As the surfactant, a variety of surfactants such as fluorine-containing surfactant, nonionic surfactant, cationic surfactant, anionic surfactant and silicone-containing surfactant may be used.

In particular, when the polymerizable composition of the present invention contains a fluorine-containing surfactant, the liquid characteristics (particularly, fluidity) of a coating solution prepared can be more enhanced and therefore, uniformity of the coating thickness and liquid saving performance can be more improved.

That is, in the case of forming a film by using a coating solution to which a polymerizable composition containing a fluorine-containing surfactant is applied, the interfacial tension between the surface to be coated and the coating solution is lowered, whereby wettability of the surface to be coated is improved and coatability on the surface to be coated is enhanced. This is effective in that even when a thin film on the order of several μm is formed with a small amount of solution, a film being reduced in the thickness unevenness and having a uniform thickness can be more successfully performed.

The fluorine content of the fluorine-containing surfactant is preferably from 3 to 40 mass%, more preferably from 5 to 30 mass%, still more preferably from 7 to 25 mass%. The fluorine-containing surfactant having a fluorine content in this range is effective in view of thickness uniformity of the coated film or liquid saving performance and also exhibits good solubility in the polymerizable composition.

Examples of the fluorine-containing surfactant include Megaface F171, Megaface F172, Megaface F173, Megaface F176, Megaface F177, Megaface F141, Megaface F142, Megaface F143, Megaface F144, Megaface R30, Megaface F437, Megaface F475, Megaface F479, Megaface F482, Megaface F554, Megaface F780, Megaface F781 (all produced by DIC Corporation), Fluorad FC430, Fluorad FC431, Fluorad FC171 (all produced by Sumitomo 3M Ltd.), Surflon S-382, Surflon SC-101, Surflon SC-103, Surflon SC-104, Surflon SC-105, Surflon SC-1068, Surflon SC-381, Surflon SC-383, Surflon S-393, Surflon KH-40 (all produced by Asahi Glass Co., Ltd.), and Solsperse 20000 (produced by The Lubrizol Corporation).

Specific examples of the nonionic surfactant include glycerol, trimethylolpropane, trimethylolethane, their ethoxylate and propoxylate (e.g., glycerol propoxylate, glycerin ethoxylate), polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene nonylphenyl ether, polyethylene glycol dilaurate, polyethylene glycol distearate, and sorbitan fatty acid esters (such as Pluronic L10, L31, L61, L62, 10R5, 17R2 and 25R2, and Tetronic 304, 701, 704, 901, 904 and 150R1, produced by BASF).

Specific examples of the cationic surfactant include a phthalocyanine derivative (EFKA-745, trade name, produced by Morishita Sangyo K.K.), organosiloxane polymer KP341 (produced by Shin-Etsu Chemical Co., Ltd.), (meth)acrylic acid (co)polymers POLYFLOW No. 75, No. 90 and No. 95 (produced by Kyoeisha Chemical Co., Ltd.), and W001 (produced by Yusho Co., Ltd.).

Specific examples of the anionic surfactant include W004, W005 and W017 (produced by Yusho Co Ltd.).

Examples of the silicone-containing 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" produced Dow Corning Toray Silicone Co., Ltd.; "TSF-4440", "TSF-4300", "TSF-4445", "TSF-4460" and "TSF-

4452" produced by Momentive Performance Materials Inc.; "KP341", "KF6001" and "KF6002" produced by Shin-Etsu Silicone; and "BYK307", "BYK-323" and "BYK-330" produced by BYK Chemie.

Among these surfactants, the fluorine-containing surfactant is more preferred.

As the surfactant, one kind of a surfactant may be used, or two or more kinds of surfactants may be used in combination.

The polymerizable composition may or may not contain a surfactant, but in the case of containing a surfactant, the content thereof is preferably from 0.001 to 1 mass%, more preferably from 0.01 to 0.1 mass%, based on the entire solid content by mass of the polymerizable composition of the present invention.

[13] Other components

In the polymerizable composition of the present invention, in addition to the above-described essential components and preferred additives, other components may be appropriately selected and used according to the purpose within the range not impairing the effects of the present invention.

Examples of other components which can be used in combination include a silane coupling agent, a heat curing accelerator, a thermal polymerization inhibitor, a plasticizer, and a colorant (colored pigment or dyestuff). Furthermore, an adherence promoter to substrate surface and other auxiliary agents (for example, an electrically conductive particle, a filler, a defoaming agent, a flame retardant, a leveling agent, a release promoter, an antioxidant, a perfume, a surface tension adjusting agent and a chain transfer agent) may be also used in combination.

By appropriately incorporating these components, the properties of the target solder resist, such as stability, photographic property and film property, can be adjusted. In particular, addition of a coupling agent is preferred for enhancing the adherence to the substrate.

The thermal polymerization inhibitor is described in detail, for example, in paragraphs [0101] and [0102] of JP-A-2008-250074.

The plasticizer is described in detail, for example, in paragraphs [0103] and [0104] of JP-A-2008-250074.

The colorant is described in detail, for example, in paragraphs [0105] and [0106] of JP-A-2008-250074 and paragraphs [0038] and [0039] of JP-A-2009-205029.

The adherence promoter is described in detail, for example, in paragraphs [0107] to [0109] of JP-A-2008-250074.

All of the additives described in these publications are usable for the polymerizable composition of the present invention.

The solid content concentration of the thus-obtained polymerizable composition of the present invention is preferably from 5 to 90 mass%, more preferably from 20 to 80 mass%, and most preferably from 40 to 60 mass%.

The polymerizable composition of the present invention is preferably filtered through a filter for the purpose of removing extraneous substances or reducing defects. A filter conventionally used for filtration and the like can be used without any particular limitation. Examples thereof include a filter formed of a fluororesin such as PTFE (polytetrafluoroethylene), a polyamide-based resin such as nylon-6 and nylon 6,6, and a polyolefin resin (including high-density polyolefin and ultrahigh molecular polyolefin) such as polyethylene and polypropylene (PP). Among these materials, polypropylene (including high-density polypropylene) is preferred.

The pore size of the filter is suitably on the order of 0.01 to 7.0 μm , preferably on the order of 0.01 to 2.5 μm , more preferably on the order of 0.01 to 1.5 μm . Within this range, fine extraneous substances which are mixed in the dissolved pigment or the like and inhibit preparation of a uniform and smooth colored composition in the later step can be unfailingly removed.

At the time of using a filter, different filters may be combined. In this case, filtration through a first filter may be performed only once or may be performed two or more times. In the case of performing filtration two or more times by using a combination of different filters, the pore size in the second and subsequent filtrations is preferably larger than the pore size of the first filtration. Also, first filters differing in the pore size within the range above may be combined. For the pore size as used herein, the nominal value of filter makers may be referred to. As for the commercially available filter, the filter may be selected from various filters offered, for example, by Nihon Pall Corporation, Advantec Toyo Kaisha, Ltd., Nihon Entegris K.K. (the former Nihon Mykrolis Corporation), and Kitz Microfilter Corporation.

As the second microfilter, a filter formed of the same material or the like as the first filter may be used. The pore size of the second filter is suitably on the order of 0.5 to 7.0 μm , preferably on the order of 2.5 to 7.0 μm , more preferably on the order of 4.5 to 6.0 μm .

Within this resin, extraneous substances which are mixed in the mixed solution and inhibit preparation of a uniform and smooth polymerizable composition in the later step can be removed while allowing the component particles contained in the mixed solution to remain.

For example, it may be possible to perform the filtering through the first filter by using only a liquid dispersion and after mixing other components, perform the filtering through the second filter.

The use application of the polymerizable composition of the present invention is not particularly limited, but examples thereof include a solder resist, a light-shielding film for back surface of a silicon substrate in a solid-state imaging device, and a light-shielding film for wafer-level lens, with a solder resist being preferred.

In the case where the polymerizable composition of the present invention is used for a solder resist, in order to form a coated film having a relatively large thickness, the solid content concentration is preferably from 30 to 80 mass%, more preferably from 35 to 70 mass%, and most preferably from 40 to 60 mass%.

The viscosity of the polymerizable composition of the present invention is preferably from 1 to 3,000 mPa·s, more preferably from 10 to 2,000 mPa·s, and most preferably from 100 to 1,500 mPa·s.

In the case where the polymerizable composition of the present invention is used for a solder resist, in view of thick film formability and uniform coatability, the viscosity is preferably from 10 to 3,000 mPa·s, more preferably from 500 to 1,500 mPa·s, and most preferably from 700 to 1,400 mPa·s.

The present invention also relates to a photosensitive layer formed of the polymerizable composition of the present invention. This photosensitive layer is formed of the polymerizable composition of the present invention and therefore, is a photosensitive layer exhibiting high light-blocking effect in the infrared region and high light transparency in the visible region and being capable of forming a pattern with excellent resolution by alkali development. Furthermore, in the case where the substrate on which the photosensitive layer is provided has an uneven shape, the photosensitive layer of the present invention is a photosensitive layer capable of having a shape successfully following the uneven shape of the substrate.

The present invention also relates to a permanent pattern formed using the polymerizable composition of the present invention. The permanent pattern of the present invention is obtained by applying exposure and alkali development to the photosensitive layer

formed of the polymerizable composition of the present invention and by virtue of using the polymerizable composition of the present invention, this is a pattern exhibiting high light-blocking effect in the infrared region and high light transparency in the visible region and being excellent in the resolution by alkali development. Furthermore, as described above, the photosensitive layer of the present invention has a shape successfully following the uneven shape of the substrate and therefore, irrespective of the site of the substrate, the thickness of the photosensitive layer can be made to take a desired value. As a result, light such as radiation in the exposure step can be allowed to reach sufficiently the deep part of the photosensitive layer in any region of the substrate, and curing by exposure can be adequately performed. Accordingly, the pattern of the present invention is a pattern reduced in separation of the pattern or generation of an adherence failure to the substrate.

In addition, the present invention also relates to a pattern forming method comprising, in order, a step of forming a photosensitive layer by using the polymerizable composition of the present invention, a step of patternwise exposing the photosensitive layer to cure the exposed area, and a step of removing the unexposed area by alkali development to form a permanent pattern.

The method for forming a permanent pattern by using the polymerizable composition of the present invention is described in detail below by referring, for example, to a patterned solder resist. However, descriptions regarding the kind and amount used of the solvent for preparation of a coating solution, the coating method of the coating solution, the thickness of the photosensitive layer, the exposure or other steps, and the like are not limited to the application to a solder resist. Here, for example, a case of forming a photosensitive layer (polymerizable composition layer) by using the polymerizable composition is described.

-Photosensitive Layer-

In order to form a patterned solder resist (solder resist pattern), a photosensitive layer is first formed using the polymerizable composition of the present invention. The photosensitive layer is not particularly limited as long as it is a layer formed by containing the polymerizable composition, and the film thickness, laminate structure and the like can be appropriately selected according to the purpose.

The method forming the photosensitive layer includes a method comprising dissolving, emulsifying or dispersing the polymerizable composition of the present invention in water or a solvent to prepare a coating solution, applying the coating solution directly on a support, and drying the coating to form the photosensitive layer.

The solvent for preparation of the coating solution is not particularly limited and may be appropriately selected according to the purpose from those capable of uniformly dissolving or dispersing respective components of the polymerizable composition of the present invention. Examples thereof include alcohols such as methanol, ethanol, normal propanol, isopropanol, normal butanol, secondary butanol and normal hexanol; ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone and diisobutyl ketone; esters such as ethyl acetate, butyl acetate, normal amyl acetate, methyl sulfate, ethyl propionate, dimethyl phthalate, ethyl benzoate, propylene glycol monomethyl ether acetate and methoxy propyl acetate; aromatic hydrocarbons such as toluene, xylene, benzene and ethylbenzene; halogenated hydrocarbons such as carbon tetrachloride, trichloroethylene, chloroform, 1,1,1-trichloroethane, methylene chloride and monochlorobenzene; ethers such as tetrahydrofuran, diethyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 1-methoxy-2-propanol and propylene glycol monomethyl ether; dimethylformamide, dimethylacetamide, dimethylsulfoxide and sulfolane. One of these solvents may be used alone, or two or more thereof may be used in combination. Also, a known surfactant may be added.

The method for applying the coating solution on a support is not particularly limited and may be appropriately selected according to the purpose, and examples thereof include a coating method using a spin coater, a slit spin coater, a roll coater, a die coater or a curtain coater.

The conditions when drying the coating vary depending on respective components, the kind of solvent, the ratio used and the like but are usually a temperature of 60 to 150°C and from 30 seconds to 15 minutes.

The thickness of the photosensitive layer is not particularly limited and may be appropriately selected according to the purpose but, for example, is preferably from 1 to 100 μm , more preferably from 2 to 50 μm , still more preferably from 4 to 30 μm .

(Solder Resist Pattern Forming Method)

The method for forming a solder resist permanent pattern by using the polymerizable composition for solder resist of the present invention comprises at least a exposure step and usually, further comprises a development step under conditions appropriately selected as needed and other steps. The term "exposure" as used in the present invention includes not only exposure to light at various wavelengths but also irradiation with radiation such as electron beam and X-ray.

<Exposure Step>

The exposure step is a step of exposing the photosensitive layer formed of the polymerizable composition layer through a mask, and in this step, only the region irradiated with light is cured.

The exposure is preferably performed by the irradiation with radiation, and examples of the radiation that can be used for exposure include a visible ray, an ultraviolet ray, a far ultraviolet ray, an electron beam, and X-ray. The radiation is preferably an electron beam, KrF, ArF, an ultraviolet ray such as g-line, h-line and i-line, or visible light. Among these, g-line, h-line and i-line are preferred.

The exposure system includes, for example, stepper exposure and exposure using a high-pressure mercury lamp.

The exposure dose is preferably from 5 to 3,000 mJ/cm², more preferably from 10 to 2,000 mJ/cm², and most preferably from 50 to 1,000 mJ/cm².

<Other Steps>

Other steps are not particularly limited and may be appropriately selected according to the purpose. Examples thereof include a step of surface-treating a base material, a development step, a curing treatment step and a post-exposure step.

<Development Step>

Following the exposure step, alkali development (development step) is performed, whereby the portion not irradiated with light in the exposure step is dissolved out into an aqueous alkali solution. As a result, only the photocured portion remains, and a patterned solder resist having light-blocking effect is formed.

The developer is preferably an organic alkali developer that does not damage the underlying circuit. The development temperature is usually from 20 to 40°C, and the development time is from 10 to 180 seconds.

As for the alkali used in the developer, for example, an aqueous alkaline solution obtained by diluting an organic alkaline compound such as aqueous ammonia, ethylamine, diethylamine, dimethylethanolamine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, choline, pyrrole, piperidine and 1,8-diazabicyclo-[5,4,0]-7-undecene with pure water to a concentration of generally from 0.001 to 10 mass%, preferably from 0.01 to 1 mass%, is used. In the case of using a developer composed of such an aqueous alkaline

solution, the film after development is generally washed (rinsed) with pure water.

<Curing Treatment Step>

The curing treatment step is a step of, after the development step is performed, if desired, applying a curing treatment to the photosensitive layer in the formed pattern, and by performing this treatment, the mechanical strength of the permanent pattern is enhanced.

The curing treatment step is not particularly limited and may be appropriately selected according to the purpose, but examples thereof include an entire surface exposure treatment and an entire surface heating treatment.

The method for the entire surface exposure treatment includes, for example, a method of, after the development step, exposing the entire surface of the laminate having the patterned photosensitive layer formed. By the entire surface exposure, curing of the polymerization components in the polymerizable composition forming the photosensitive layer is promoted, and curing of the permanent pattern further proceeds, whereby the mechanical strength and durability are improved.

The apparatus used for performing the entire surface exposure is not particularly limited and may be appropriately selected according to the purpose. Preferred examples thereof include an UV exposure machine such as ultrahigh-pressure mercury lamp.

The method for the entire surface heating treatment includes a method of, after the development step, heating the entire surface of the laminate having the patterned photosensitive layer formed. By the entire surface heating, the film strength of the pattern is increased.

The heating temperature in the entire surface heating is preferably from 120 to 250°C, more preferably from 140 to 220°C. When the heating temperature is 120°C or more, the film strength is increased by the heating treatment, and when it is 250°C or less, the film quality can be prevented from becoming weak and brittle due to decomposition of the resin in the photopolymerizable composition.

The heating time in the entire surface heating is preferably from 3 to 180 minutes, more preferably from 5 to 120 minutes.

The apparatus used for performing the entire surface heating is not particularly limited and may be appropriately selected according to the purpose from conventional apparatuses. Examples thereof include a dry oven, a hot plate and an IR heater.

The thus-formed patterned resist has an excellent infrared-blocking effect and therefore, has a wide range of application. The polymerizable composition of the present

invention has an excellent light-blocking effect in the infrared region and light transparency in the ultraviolet to visible region, so that a pattern having an excellent profile can be formed. At the same time, the pattern (cured film) formed has an excellent infrared-blocking effect and in turn, is useful in forming a solder resist for a device with a photodiode having sensitivity even to the infrared region, particularly, a solid-state imaging device.

As described above, the polymerizable composition of the present invention is useful for the formation of not only a solder resist but also a light-blocking film for back surface of a silicon substrate in a solid-state imaging device, or a light-blocking film for wafer-level lens.

In this way, the present invention also relates to a solid-state imaging device having a permanent pattern formed of the polymerizable composition of the present invention.

The solid-state imaging device according to an embodiment of the present invention is described below by referring to Figs. 1 and 2, but the present invention is not limited the following specific example.

Incidentally, common numerical references are used for the portions common between Fig. 1 and Fig. 2.

Also, in the description, the "top", "above" and "upper side" indicate the side farther from the silicon substrate 10, and the "bottom", "below" and "lower side" indicate the side closer to the silicone substrate 10.

Fig. 1 is a schematic cross-sectional view showing a configuration of a camera module having a solid-state imaging device according to a specific example of the one embodiment above.

In Fig. 1, the camera module 200 is connected to a circuit substrate 70 as a package substrate through a solder ball 60 as a connection member.

In detail, the camera module 200 is configured to include a solid-state imaging device substrate 100 having an imaging element part on the first major surface of a silicon substrate, a glass substrate 30 (light transmitting substrate) disposed above the first major surface of the solid-state imaging device substrate 100, an infrared cut filter 42 disposed above the glass substrate 30, a lens holder 50 being disposed above the glass substrate 30 and the infrared cut filter 42 and having an imaging lens 40 in the internal space, and a light-blocking and electromagnetic shield 44 disposed to surround the peripheries of the solid-state imaging device substrate 100 and the glass substrate 30. Each member is bonded through an adhesive 20, 41, 43 or 45.

In the camera module 200, incident light $h\nu$ from the outside sequentially passes through the imaging lens 40, the infrared cut filter 42 and the glass substrate 30 and reaches the imaging device part of the solid-state imaging device substrate 100.

Also, the camera module 200 is connected to a circuit substrate 70 through a solder ball 60 (connection material) on the second major surface side of the solid-state imaging device substrate 100.

Fig. 2 is a cross-sectional view on an enlarged scale showing the solid-state imaging device substrate 100 in Fig. 1.

The solid-state imaging device substrate 100 is configured to include a silicon substrate 10 as a base body, an imaging element 12, an interlayer insulating film 13, a base layer 14, a red color filter 15R, a green color filter 15G, a blue color filter 15B, an overcoat 16, a microlens 17, a light-blocking film 18, an insulating film 22, a metal electrode 23, a solder resist layer 24, an internal electrode 26, and a device surface electrode 27.

The solder resist layer 24 may be omitted.

First, the configuration on the first major surface side of a solid-state imaging device substrate 100 is mainly described.

As shown in Fig. 2, an imaging element part where a plurality of imaging elements 12 such as CCD and CMOS are two-dimensionally arranged is provided on the first major surface side of a silicon substrate 10 that is the base body of the solid-state imaging device substrate 100.

An interlayer insulating film 13 is formed on the imaging element 12 in the imaging element part, and a base layer 14 is formed on the interlayer insulating film 13. Furthermore, a red color filter 15R, a green color filter 15G and a blue color filter 15B (hereinafter sometimes collectively referred to as "color filter 15") are disposed on the base layer 14 to correspond to respective imaging elements 12.

A light-blocking film not shown may be provided in the boundaries of the red color filter 15R, the green color filter 15G and the blue color filter 15B and in the peripheries of the imaging element part. This light-blocking film can be produced, for example, by using a known black color resist.

An overcoat 16 is formed on the color filter 15, and a microlens 17 is formed on the overcoat 16 to correspond to the imaging element 12 (color filter 15).

A peripheral circuit (not shown) and an internal electrode 26 are provided in the periphery of the imaging element part on the first major surface side, and the internal electrode

26 is electrically connected to the imaging element 12 through the peripheral circuit.

Furthermore, a device surface electrode 27 is formed on the internal electrode 26 through the interlayer insulating film 13, and in the interlayer insulating film 13 between the internal electrode 26 and the device surface electrode 27, a contact plug (not shown) for electrically connecting these electrodes is formed. The device surface electrode 27 is used, for example, for applying a voltage or reading a signal through the contact plug and the internal electrode 26.

A base layer 14 is formed on the device surface electrode 27, and an overcoat 16 is formed on the base layer 14. The base layer 14 and the overcoat 16 formed on the device surface electrode 27 are opened to form a pad opening part, and a part of the device surface electrode 27 is thereby exposed.

This is the configuration on the first major surface side of the solid-state imaging device substrate 100.

On the first major surface side of the solid-state imaging device substrate 100, an adhesive 20 is provided in the periphery of the imaging element part, and the solid-state imaging device substrate 100 and the glass substrate 30 are bonded through the adhesive 20.

Also, the silicon substrate 10 has a through hole penetrating the silicon substrate 10, and a through-electrode as a part of a metal electrode 23 is provided inside the through hole. The imaging element part and a circuit substrate 70 are electrically connected by the through-electrode.

The configuration on the second major surface side of the solid-state imaging device substrate 100 is mainly described below.

On the second major surface side, an insulating film 22 is formed over an area from the second major surface to the inner wall of the through hole.

A metal electrode 23 patterned to extend from the region on the second major surface of the silicon substrate 10 to the inside of the through hole is provided on the insulating film 22. The metal electrode 23 is an electrode for connection between the imaging element part in the solid-state imaging device substrate 100 and a circuit substrate 70.

Out of this metal electrode 23, the portion formed inside the through hole is the through-electrode. The through-electrode penetrates a part of the silicon substrate 10 and the interlayer insulating film to reach below the internal electrode 26 and electrically connected to the internal electrode 26.

Furthermore, on the second major surface side, a solder resist layer 24 (protective

insulating film) covering the second major surface on which the metal electrode 23 is formed, and having an opening part exposing a part of the metal electrode 23, is provided.

In addition, on the second major surface side, a light-blocking film 18 covering the second major surface on which the solder resist layer 24 is formed, and having an opening part exposing a part of the metal electrode 23, is provided.

In this configuration, (1) a light-blocking solder resist layer where the light-blocking film 18 and the solder resist layer 24 are united into a single layer may be formed of the polymerizable composition of the present invention, or (2) while the light-blocking layer 18 and the solder resist layer 24 are separate layers, the light-blocking film 18 may be formed of the polymerizable composition of the present invention (in this case, the solder resist layer may be formed of a known solder resist composition).

Incidentally, in Fig. 2, the light-blocking film 18 is patterned to cover a part of the metal electrode 23 and expose the remaining portion but may be patterned to expose the entirety of the metal electrode 23 (the same applies to the patterning of the solder resist layer 24).

Also, the solder resist layer 24 may be omitted, or the light-blocking film 18 may be formed directly on the second major surface where the metal electrode 23 is formed.

A solder ball 60 as a connection member is provided on the exposed metal electrode 23, and the metal electrode 23 of the solid-state imaging device substrate 100 and the connection electrode not shown of the circuit substrate 70 are electrically connected through the solder ball 60.

In the above, the configuration of the solid-state device substrate 100 is described, but each part except for the light-blocking film 18 of the solid-state imaging device substrate 100 can be formed by a known method such as method described in paragraphs 0033 to 0068 of JP-a-2009-158863 and method described in paragraphs 0036 to 0065 of JP-A-2009-99591.

The light-blocking film 18 can be formed by the above-described production method for the light-blocking film of the present invention.

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

The color filter 15 is formed, for example, by photolithography using a known color resist.

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

The microlens 17 is formed, for example, by photolithography using a styrene-based resin or the like.

In the case where the solder resist layer 24 and the light-blocking layer 18 are combined to form a light-blocking solder resist layer as a single layer, the layer is preferably formed of the polymerizable composition of the present invention.

On the other hand, when the solder resist layer 24 and the light-blocking film 18 are separate layers, the solder resist layer 24 is preferably formed, for example, by photolithography using a known solder resist containing a phenolic resin, a polyimide-based resin or an amine-based resin.

The solder ball 60 is formed, for example, using Sn-Pb (eutectic), 95Pb-Sn (high-lead high-melting-point solder) or a Pb-free solder such as Sn-Ag, Sn-Cu and Sn-Ag-Cu. The solder ball 60 is formed, for example, as a sphere having a diameter of 100 to 1,000 μm (preferably a diameter of 150 to 700 μm).

The internal electrode 26 and the device surface electrode 27 are formed as a metal electrode such as Cu, for example, by CMP (chemical mechanical polishing), photolithography or etching.

The metal electrode 23 is formed as a metal electrode such as Cu, Au, Al, Ni, W, Pt, Mo, Cu compound, W compound and Mo compound, for example, by sputtering, photolithography, etching or electrolytic plating. The metal electrode 23 may be in a single-layer configuration or a multilayer configuration consisting of two or more layers.

The film thickness of the metal electrode 23 is, for example, from 0.1 to 20 μm (preferably from 0.1 to 10 μm). The silicon substrate 10 is not particularly limited, but a silicon substrate reduced in the thickness by shaving the back surface of the substrate may be used. The thickness of the substrate is not limited, but, for example, a silicon wafer having a thickness of 20 to 200 μm (preferably from 30 to 150 μm) is used.

The through hole of the silicon substrate 10 is formed, for example, by photolithography and RIE (reactive ion etching).

In the forgoing pages, the solid-state imaging device substrate 100 as a specific example of the above-described one embodiment is described by referring to Figs. 1 and 2, but the one embodiment is not limited to the mode of Fig. 1 and Fig. 2, and the configuration of the embodiment is not particularly limited as long as it is a configuration having a metal electrode and a light-blocking film on the back surface side.

Next, an example where the permanent pattern obtained using the polymerizable

composition of the present invention is applied to the light-blocking film of a wafer-level lens is described below by referring to the drawings.

Fig. 3 is a plan view showing one example of the configuration of a wafer-level lens array having a plurality of wafer-level lenses.

As shown in Fig. 3, the wafer-level lens array has a substrate 410 and lenses 412 arranged on the substrate 410. Here, in Fig. 3, a plurality of lenses 412 are two-dimensionally arranged with respect to the substrate 410 but may be one-dimensionally arranged.

Fig. 4 is a cross-sectional view along line A-A in Fig. 3.

As shown in Fig. 4, in the wafer-level lens array, a light-blocking film 414 for preventing light transmission through a portion except for the lens 412 is provided between a plurality of lenses 412 arranged on the substrate 410.

The wafer-level lens is composed of one lens 412 present on the substrate 410 and a light-blocking film 414 provided in the circumferential periphery thereof. The polymerizable composition of the present invention is used for formation of this light-blocking film 414.

The wafer-level lens is described below by referring, for example, to a configuration where, as shown in Fig. 3, a plurality of lenses 412 are two-dimensionally arranged with respect to a substrate 410.

The lens 412 is generally composed of the same material as the substrate 410 and is molded integrally on the substrate 410 or is molded as a separate structure and fixed on the substrate. Here, an example is described, but the wafer-level lens is not limited to this embodiment and may take various embodiments such as a wafer-level lens having a multilayer structure or a wafer-level lens separated into a lens module by dicing.

The material forming the lens 412 includes, for example, glass. There are an abundant variety of glasses, and since glass having a high refractive index can be selected, this is suitable as the material of the lens. Also, the glass is excellent in the heat resistance and has the advantage of withstanding the reflow mounting on an imaging unit or the like.

Other materials for forming the lens 412 include a resin. The resin is excellent in the processability and is suitable for simply and inexpensively forming a lens surface by a mold or the like.

In this case, an energy-curable resin is preferably used for formation of the lens 412. The energy-curable resin may be either a resin capable of curing by heat or a resin capable of curing by irradiation with an active energy ray (for example, irradiation with heat, ultraviolet

ray or electron beam).

As the energy-curable resin, all of known resins may be used, but in consideration of reflow mounting of the imaging unit, a resin having a relatively high softening point, for example, a softening point of 200°C or more is preferred. A resin having a softening point of 250°C or more is more preferred.

The mode and production of the wafer-level lens are specifically described below by referring, for example, to the production method of a wafer-level lens array based on Figs. 5 to 10.

[Mode and Production (1) of Wafer-Level Lens]

-Formation of Lens-

The method for forming a lens 412 on a substrate 410 is described by referring to Fig. 5 and Figs. 6A to 6C.

Fig. 5 is a view showing how a molding material (indicated by M in Fig. 5) as a resin composition for lens formation is supplied to a substrate 410.

Also, Figs. 6A to 6C are views showing the procedure of molding a lens 412 on a substrate 410 by using a mold 460.

As shown in Fig. 5, a molding material M is dropped on a lens 412 molding site of a substrate 410 by using a dispenser 450. Here, a molding material M in an amount corresponding to one lens 412 is supplied to one site to be fed.

After supplying the molding material M to the substrate 410, as shown in Fig. 6A, a mold 460 for molding lenses 412 is disposed on the substrate 410 surface side to which the molding material M is supplied.

In the mold 460, concaves 462 for transferring the lens 412 shape are provided according to the desired number of lenses 412.

As shown in Fig. 6B, the mold 460 is pressed against the molding material M on the substrate 410 to deform the molding material M along the lines of the concave 462 shape. In the state of the mold 460 being pressed against the molding material M, when the molding material M is a thermosetting resin or an ultraviolet-curable resin, the mold 460 is externally irradiated with heat or ultraviolet ray to cure the molding material M.

After curing the molding material M, as shown in Fig. 6C, the substrate 410 and lenses 412 are separated from the mold 460.

-Formation of Light-Blocking Film-

The method for forming a light-blocking film 414 in the circumferential periphery of

the lens 412 is described below by referring to Figs. 7A to 7C.

Figs. 7A to 7C are schematic cross-sectional views showing the process of providing a light-blocking film 414 on the substrate 410 having molded thereon lenses 412.

The method for forming the light-blocking film 414 includes a light-blocking coating layer forming step of coating the polymerizable composition of the present invention on a substrate 410 to form a light-blocking coating layer 414A (see, Fig. 7A), an exposure step of pattern-exposing the light-blocking coating layer 414A through a mask 470 (see, Fig. 7B), and a development step of developing the light-blocking coating layer 414A after exposure to remove the uncured area and form a patterned light-blocking film 414 (see, Fig. 7C).

Incidentally, formation of the light-blocking film 414 can be arbitrarily performed before producing the lens 412 or after the lens 412 is produced, but here, the method of performing the formation after production of the lens 412 is described in detail.

The steps in the method of forming the light-blocking film 414 are described below.

<Light-Blocking Coating Layer Forming Step>

In the light-blocking coating layer forming step, as shown in Fig. 7A, a polymerizable composition is coated on a substrate 410 to form a light-blocking coating layer 414A having low optical reflectance and being composed of the polymerizable composition. At this time, the light-blocking coating layer 414A is formed to cover all of the substrate 410 surface and the lens surface 412a and lens edge 412b surface of the lens 412.

The substrate 410 which can be used in this step is not particularly limited. Examples thereof include soda glass, alkali-free glass, Pyrex (registered trademark) glass, quartz glass and transparent resin.

The substrate 410 as used herein indicates an embodiment containing both the lens 412 and the substrate 410 in the case of integrally forming the lens 412 and the substrate 410.

On the substrate 410, if desired, an undercoat layer may be provided so as to improve adherence to an overlying layer, prevent diffusion of the material, or flatten the substrate 410 surface.

As the method for coating the polymerizable composition on the substrate 410 and the lens 412, various coating methods such as slit coating, spray coating, inkjet printing, spin coating, cast coating, roll coating and screen printing may be applied.

In view of thickness uniformity of the coated film and easy drying of the coating solvent, the film thickness immediately after coating of the polymerizable composition is preferably from 0.1 to 10 μm , more preferably from 0.2 to 5 μm , still more preferably from 0.2

to 3 μm .

Drying (prebaking) of the light-blocking coating layer 414A coated on the substrate 410 may be performed using a hot plate, an oven or the like at a temperature of 50 to 140°C for 10 to 300 seconds.

The thickness of the coated film after drying of the polymerizable composition (hereinafter, sometimes referred to as "dry thickness") may be arbitrarily selected by taking into consideration the performance such as desired light-blocking effect and is generally from 0.1 μm to less than 50 μm .

<Exposure Step>

In the exposure step, the light-blocking coating layer 414A formed in the light-blocking coating layer forming step is pattern-exposed. The pattern exposure may be scanning exposure, but an embodiment of, as shown in Fig. 7B, performing the exposure through a mask 470 having a predetermined mask pattern is preferred.

As for the exposure in this step, the pattern exposure of the light-blocking coating layer 414A is performed by exposure through a predetermined mask pattern, where only the portion irradiated with light out of the light-blocking coating layer 414A is cured by the exposure. In this exposure, a mask pattern allowing for irradiation with light on the lens edge 412b surface and the substrate 410 surface between lenses 412 is used. By using such a mask pattern, the light-blocking coating layer 414A only in the region excluding the lens surface 412a is cured by the irradiation with light, and the cured region forms the light-blocking film 414.

The radiation which can be used for exposure is preferably an ultraviolet ray such as g-line, h-line and i-line. For this radiation, a light source having a single wavelength may be used, or a light source containing all wavelengths, such as high-pressure mercury lamp, may be used.

<Development Step>

Subsequently, alkali development (development step) is performed, whereby the portion not irradiated with light in the exposure, that is, the uncured region of the light-blocking coating layer 414A, is dissolved out into an aqueous alkali solution and only the region cured by the irradiation with light is allowed to remain.

Specifically, by developing the light-blocking coating layer 414A exposed as shown in Fig. 7B, only the light-blocking coating layer 414A formed on the lens surface 12a is, as

shown in Fig. 7C, removed and a light-blocking film 414 cured is formed in other regions.

As the alkali agent contained in the developer (aqueous alkaline solution) used in the development step, all of an organic alkali agent, an inorganic alkali agent and a combination thereof may be used. For the light-blocking film formation in the present invention, an organic alkali agent is preferably used, because it scarcely damages the neighboring circuit or the like.

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

The development temperature is usually from 20 to 30°C, and the development time is from 20 to 90 seconds.

In the case of using a developer composed of such an aqueous alkaline solution, after removing the unexposed area of the coated film with a developer, the film is generally washed (rinsed) with pure water. That is, after the development, the film is thoroughly washed with pure water to remove the excess developer and then further subjected to a drying step.

Incidentally, after performing the above-described light-blocking coating layer forming step, exposure step and development step, a curing step of curing the formed light-blocking film (light-blocking pattern) by heating (post-baking) and/or exposure may be provided, if desired.

The post-baking is a heating treatment after development so as to achieve complete curing, and a thermal curing treatment usually at 100 to 250°C is performed. The conditions of post-baking, such as temperature and time, may be appropriately set according to the material of the substrate 410 or lens 412. For example, when the substrate 412 is glass, out of the temperature range above, a temperature of 180 to 240°C is preferably used.

This post-baking treatment is applied to the light-blocking film 414 formed after development and can be performed in a continuous system or a batch system by using a heating device such as hot plate, convection oven (hot air circulating drier) and high-frequency

heater to establish the above-described conditions.

The procedure above is described by referring, for example, a case where the lens 412 has a concave shape, but the shape is not particularly limited and may be convex or aspheric. Also, the procedure above is described by referring, for example, a wafer-level lens where a plurality of lenses 412 are molded on one surface of a substrate 410, but a configuration where a plurality of lenses 412 are molded on both surfaces of a substrate 410 may be also employed and in this case, the patterned light-blocking film 414 is formed on both surfaces in the regions excluding lens surfaces.

[Mode and Production (2) of Wafer-Level Lens]

Fig. 8 is a view showing another configuration example of the wafer-level lens array.

The wafer-level lens shown in Fig. 8 is in a configuration (monolithic type) where the substrate 410 and the lens 412 are simultaneously molded using the same molding material.

As the molding material for the preparation of such a wafer-level lens, the same as those described above may be used. Also, in this example, a plurality of concave lenses 412 are formed on one surface (surface on the upper side in the Figure) of a substrate 410, and a plurality of convex lenses 420 are formed on another surface (surface on the lower side in the Figure). Furthermore, a patterned light-blocking film 414 is formed in the regions excluding lens surfaces 412a of the substrate 410, that is, formed on the substrate 410 surface and the lens edge 412b surface. As the patterning method when forming the light-blocking film 414, the above-described procedure may be applied.

[Mode and Production (3) of Wafer-Level Lens]

Still another configuration example of the wafer-level lens array and the production procedure therefor are described below by referring to Figs. 9A to 9C and Figs. 10A to 10C.

Figs. 9A to 9C are schematic views showing another process of forming a patterned light-blocking film 414.

Figs. 10A to 10C are schematic views showing the process of first forming a patterned light-blocking film 414 and next molding a lens 412.

In the example of the wafer-level lens array shown in Figs. 5 to 8, a patterned light-blocking film 414 is formed on a substrate 410 having provided thereon a lens 412, but in the following procedure, a patterned light-blocking film 414 is first formed on a substrate 410 and a lens 412 is then molded on the substrate 410.

-Formation of Light-Blocking Film-

As shown in Fig. 9A, first, a light-blocking coating layer forming step of coating a

polymerizable composition on a substrate 410 to form a light-blocking coating layer 414A is performed.

Thereafter, drying of the light-blocking coating layer 414A formed on the substrate 410 is performed using a hot plate, an oven or the like at a temperature of 50 to 140°C for 10 to 300 seconds. The dry thickness of the polymerizable composition may be arbitrarily selected according to the performance such as desired light-blocking effect but is generally from 0.1 μm to less than 50 μm .

Next, as shown in Fig. 9B, an exposure step of patternwise exposing the light-blocking coating layer 414A formed in the light-blocking coating layer forming step, through a mask 470 is performed. The mask 470 has a predetermined mask pattern.

In the exposure of this step, the light-blocking coating layer 414 is pattern-exposed, whereby only the portion irradiated with light out of the light-blocking coating layer 414A is cured. Here, a mask pattern allowing for irradiation with light only on the light-blocking coating layer 414A in the region excluding the site working out to a lens opening 414a of a lens 412 when the lens 412 is molded in the later step, is used. By this method, the light-blocking coating layer 414A only in the region excluding the site working out to a lens opening 414a of a lens 412 is cured by the irradiation with light. As for the radiation which can be used for the exposure, an ultraviolet ray such as g-line, h-line and i-line is preferably used, similarly to the procedure described earlier.

Subsequently, alkali development (development step) is performed, whereby the light-blocking coating layer 414A only in the region corresponding to a lens opening 414a of a lens 412, which is the light-blocking coating layer 414A region uncured in the pattern exposure above, is dissolved out into an aqueous alkali solution. At this time, as shown in Fig. 9C, the photocured light-blocking coating layer 414A in the region excluding the region for a lens opening 414a of a lens 412 remains on the substrate 410 and forms a light-blocking film 414.

As for the alkali agent in the aqueous alkali solution that is the developer, the same as in the procedure described earlier may be used.

After the development, the excess developer is removed by washing, and the film is then dried.

Also in this embodiment, after performing the above-described light-blocking coating layer forming step, exposure step and development step, a curing step of curing the formed light-blocking film by post-baking and/or exposure may be provided, if desired.

The polymerizable composition of the present invention can be easily cleaned and removed with a known cleaning solution even when it attaches, for example, to a nozzle at the discharge port of the coating apparatus, a piping area of the coating apparatus, or the interior of the coating apparatus. In this case, in order to more efficiently perform the cleaning and removal, a solvent described above as the solvent contained in the polymerizable composition of the present invention is preferably used for the cleaning solution.

Furthermore, cleaning solutions described, for example, in JP-A-7-128867, JP-A-7-146562, JP-A-8-278637, JP-A-2000-273370, JP-A-2006-85140, JP-A-2006-291191, JP-A-2007-2101, JP-A-2007-2102 and JP-A-2007-281523 may be also suitably used as the cleaning solution for cleaning and removing the polymerizable composition of the present invention.

As the cleaning solution, an alkylene glycol monoalkyl ether carboxylate or an alkylene glycol monoalkyl ether is preferably used.

One of these solvent usable as the cleaning solution may be used alone, or two or more thereof may be mixed and used.

In the case of mixing two or more solvents, a mixed solvent obtained by mixing a hydroxyl group-containing solvent and a hydroxyl group-free solvent is preferred. The mass ratio between the hydroxyl group-containing solvent and the hydroxyl group-free solvent is from 1/99 to 99/1, preferably from 10/90 to 90/10, more preferably from 20/80 to 80/20. The mixed solvent is preferably a mixed solvent of propylene glycol monomethyl ether acetate (PGMEA, another name: 1-methoxy-2-acetoxyp propane) and propylene glycol monomethyl ether (PGME, another name: 1-methoxy-2-propanol) in a ratio of 60/40.

Incidentally, in order to enhance the permeability of the cleaning solution into the polymerizable composition, a surfactant described above as the surfactant which can be incorporated into the polymerizable composition may be added to the cleaning solution.

-Formation of Lens-

A step of forming a lens 412 after the formation of the light-blocking film 414 is described below.

As shown in Fig. 10A, a molding material M constituting the lens 412 is dropped by a dispenser 450 on the substrate 410 having formed thereon the patterned light-blocking film 414. The molding material M is supplied to cover the region corresponding to a lens opening 414a of a lens 412, including a part of the light-blocking film 414 edge adjacent to the opening.

After supplying the molding material M to the substrate 410, as shown in Fig. 10B, a mold 480 for molding lenses is disposed on the substrate 410 surface side to which the

molding material M is supplied. In the mold 480, concaves 482 for transferring the lens 412 shape are provided according to the desired number of lenses 412.

The mold 480 is pressed against the molding material M on the substrate 410 to deform the molding material M along the lines of the concave shape. In the state of the mold 480 being pressed against the molding material M, when the molding material M is a thermosetting resin or an ultraviolet-curable resin, the mold is externally irradiated with heat or ultraviolet ray to cure the molding material M.

After curing the molding material M, the substrate 410 and lenses 412 are separated from the mold 480 to obtain a wafer-level lens having, as shown in Fig. 10C, a patterned light-blocking film 414 on a substrate 410.

In this way, the wafer-level lens may have not only a configuration where the patterned light-blocking film 414 is provided, as shown in Fig. 7, in the region excluding a lens surface 412a of a lens 412, but also a configuration where the light-blocking film 414 is provided, as shown in Fig. 10C, in the region excluding a lens opening 414a of a lens 412.

In the wafer-level lens, the light-blocking film 414 being patternwise formed on at least one surface of the substrate 410 sufficiently blocks light in the regions excluding the lens surface 412a or lens opening 414a of the 412 and at the same time, suppress the generation of reflected light. Accordingly, when the wafer-level lens is applied to an imaging module with a solid-state imaging device, a trouble such as ghost or flare associated with reflected light can be prevented from occurring during imaging.

Also, the light-blocking film 414 is provided on the substrate surface, eliminating the need to fix a separate light-blocking member or the like on the wafer-level lens, and the rise in the production cost can be suppressed.

Incidentally, in the case of a configuration where a structure with an uneven surface is provided around the lens, a trouble such as ghost may be likely to occur due to reflection or diffusion of light incident on the structure. To get rid of this trouble, when a configuration of, as shown in Fig. 7, providing a patterned light-blocking film 414 in the region excluding a lens surface 412a of a lens 412 is employed, light can be blocked except for the lens surface 412a and the optical performance can be improved.

[Examples]

The present invention is described below by referring to Examples, but the present invention is not limited to these Examples by any means.

<Preparation of Binder Solution A>

A 1,000 mL-volume three-neck flask was charged with 159 g of 1-methoxy-2-propanol and heated to 85°C under nitrogen flow, and a solution prepared by adding 63.4 g of benzyl methacrylate, 72.3 g of methacrylic acid ($pK_a=4.8$) and 4.15 g of V-601 (produced by Wako Pure Chemical Industries, Ltd.) to 159 g of 1-methoxy-2-propanol was added dropwise thereto over 2 hours. After the completion of dropwise addition, the mixture was further heated for 5 hours and thereby reacted.

Subsequently, the heating was stopped, and a benzyl methacrylate/methacrylic acid copolymer (30/70 by mol) was obtained.

Thereafter, 120.0 g out of the copolymer solution was transferred to a 300 mL-volume three-neck flask, and 16.6 g of glycidyl methacrylate and 0.16 g of p-methoxyphenol were added and dissolved by stirring. After the dissolution, 3.0 g of triphenylphosphine was added, and the mixture was heated to 100°C, thereby performing an addition reaction. Disappearance of glycidyl methacrylate was confirmed by gas chromatography, and heating was stopped. Furthermore, 38 g of 1-methoxy-2-propanol was added to prepare Binder Solution A having an acid group content of 2 meq/g (acid value: 112 mgKOH/g), a crosslinking group content of 2.23 meq/g, a mass average molecular weight of 24,000 (in terms of polystyrene by GPC method) and a solid content of 46 mass%.

<Preparation of Binder Solution B>

VP-2500 [poly(p-vinylphenol) produced by Nippon Soda Co., Ltd. (mass average molecular weight: 3,500, polydispersity: 1.39)] (pK_a of p-vinylphenol: 9.9) was dissolved in propylene glycol monomethyl ether acetate to prepare Binder Solution B having a solid content of 46 mass%.

<Preparation of Binder Solution C>

1-Methoxy-2-propanol was additionally added to CYCLOMER P ACA230AA [a 1-methoxy-2-propanol solution (solid content: 55 mass%) of an acryl polymer having a carboxyl group and an unsaturated group, produced by Daicel Chemical Industries, Ltd. (mass average molecular weight: 14,000, acid value: 21 mgKOH/g); pK_a of the monomer corresponding to the carboxyl group-containing repeating unit in the acryl polymer: 4.8] to prepare Binder Solution C having a solid content of 46 mass%.

<Preparation of Binder Solution D>

A 1,000 mL-volume three-neck flask was charged with 159 g of 1-methoxy-2-propanol and heated to 85°C under nitrogen flow, and a solution prepared by adding 63.4 g of benzyl methacrylate, 72.3 g of methacrylic acid and 4.15 g of V-601 (produced by Wako Pure Chemical Industries, Ltd.) to 159 g of 1-methoxy-2-propanol was added dropwise thereto over 2 hours. After the completion of dropwise addition, the mixture was further heated for 5 hours and thereby reacted.

Subsequently, the heating was stopped, and a benzyl methacrylate/methacrylic acid copolymer (30/70 by mol) was obtained.

Thereafter, 120.0 g out of the copolymer solution was transferred to a 300 mL-volume three-neck flask, and 48.6 g of glycidyl methacrylate and 0.16 g of p-methoxyphenol were added and dissolved by stirring. After the dissolution, 3.0 g of triphenylphosphine was added, and the mixture was heated to 100°C, thereby performing an addition reaction. Progress of the reaction was confirmed by the measurement of the acid value, and when the acid value became 0, the heating was stopped. Thereto, 1-methoxy-2-propanol was added to prepare Binder Solution D having an acid group content of 0 meq/g (acid value: 0 mgKOH/g) and a solid content of 46 mass%.

<Preparation of Inorganic Filler Liquid Dispersion 1>

30 Parts by mass of silica (SO-C1, produced by Admatechs Company Limited) (inorganic filler) and 48.2 parts by mass of Binder Solution A were previously mixed, and the mixture obtained was dispersed using zirconia beads of 1.0 mm in diameter by a motor mill, M-50 (manufactured by Eiger), at a circumferential velocity of 9 m/s for 1.5 hours to prepare Inorganic Filler Liquid Dispersion 1.

<Preparation of Inorganic Filler Liquid Dispersion 2>

30 Parts by mass of silica (SO-C1, produced by Admatechs Company Limited) (inorganic filler) and 48.2 parts by mass of Binder Solution C were previously mixed, and the mixture obtained was dispersed using zirconia beads of 1.0 mm in diameter by a motor mill, M-50 (manufactured by Eiger), at a circumferential velocity of 9 m/s for 1.5 hours to prepare Inorganic Filler Liquid Dispersion 2.

<Preparation of Inorganic Filler Liquid Dispersion 3>

30 Parts by mass of silica (SO-C1, produced by Admatechs Company Limited) (inorganic filler) and 48.2 parts by mass of Binder Solution D were previously mixed, and the mixture obtained was dispersed using zirconia beads of 1.0 mm in diameter by a motor mill, M-50 (manufactured by Eiger), at a circumferential velocity of 9 m/s for 1.5 hours to prepare Inorganic Filler Liquid Dispersion 3.

<Preparation of Inorganic Filler Liquid Dispersion 4>

30 Parts by mass of silica (SO-C1, produced by Admatechs Company Limited) (inorganic filler) and 48.2 parts by mass of Binder Solution B were previously mixed, and the mixture obtained was dispersed using zirconia beads of 1.0 mm in diameter by a motor mill, M-50 (manufactured by Eiger), at a circumferential velocity of 9 m/s for 1.5 hours to prepare Inorganic Filler Liquid Dispersion 4.

<Preparation of Polymerizable Composition Solution>

(Example 1)

The components in the following formulation were mixed, and the mixture was filtered through a first filter and subsequently through a second filter to obtain the polymerizable composition solution of Example 1.

Profile Star produced by Nihon Pall Corporation (polypropylene, filtration accuracy: 1.5 μm) was used for the first filter, and HDCII produced by Nihon Pall Corporation (high-density polypropylene, filtration accuracy: 6.0 μm) was used for the second filter.

Binder Solution A (alkali-soluble binder)	14.9 parts by mass
Dipentaerythritol hexaacrylate (KAYARAD DPHA, trade name, produced by Nippon Kayaku Co., Ltd.) (polymerizable compound)	7.72 parts by mass
Irgacure 907 (an acetophenone-based compound produced by BASF Japan) (polymerization initiator)	2.03 parts by mass
Kayacure DETX-S (a thioxanthone-based compound produced by Nippon Kayaku Co., Ltd.) (sensitizer)	0.43 parts by mass

Inorganic Filler Liquid Dispersion 1 (inorganic filler)	45.09 parts by mass
Megaface F-780 (produced by DIC Corporation) (surfactant)	0.14 parts by mass
YMF-02 (produced by Sumitomo Metal Mining Co., Ltd., cesium tungsten oxide (a 18.5 mass% liquid dispersion of $\text{Cs}_{0.33}\text{WO}_3$ (average dispersed particle diameter: 800 nm or less))	26.97 parts by mass

(Example 2)

The composition of Example 2 was prepared in the same manner as in Example 1 except for further adding 5.0 parts by mass of ESPEL 9940A (an elastomer produced by Hitachi Chemical Co., Ltd.) to the polymerizable composition solution of Example 1.

(Example 3)

The composition of Example 3 was prepared in the same manner as in Example 2 except for changing Binder Solution A to Binder Solution C in Example 2.

(Example 4)

The composition of Example 4 was prepared in the same manner as in Example 2 except for changing Binder Solution A to Binder Solution B in Example 2.

(Example 5)

The composition of Example 5 was prepared in the same manner as in Example 3 except for changing Inorganic Filler Liquid Dispersion 1 to Inorganic Filler Liquid Dispersion 2 in Example 3.

(Example 6)

The following composition was mixed to obtain the polymerizable composition solution of Example 6.

Binder Solution C (alkali-soluble binder)	14.9 parts by mass
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Tricyclodecanedimethanol diacrylate (A-DCP, trade name, manufacturer: Shin-Nakamura Chemical Co., Ltd.) (polymerizable compound)	7.72 parts by mass
Irgacure 907 (an acetophenone-based compound produced by BASF Japan) (polymerization initiator)	2.03 parts by mass
Kayacure DETX-S (a thioxanthone-based compound produced by Nippon Kayaku Co., Ltd.) (sensitizer)	0.43 parts by mass
Inorganic Filler Liquid Dispersion 2 (inorganic filler)	45.09 parts by mass
Megaface F-780 (produced by DIC Corporation) (surfactant)	0.14 parts by mass
YMF-02 (produced by Sumitomo Metal Mining Co., Ltd., cesium tungsten oxide (a 18.5 mass% liquid dispersion of Cs _{0.33} WO ₃ (average dispersed particle diameter: 800 nm or less))	26.97 parts by mass
Silane coupling agent (KBM-503, produced by Shin-Etsu Chemical Co.)	3.5 parts by mass
Ultraviolet absorber (CAS No.: 98835-90-6, produced by Daito Chemical Co., Ltd.)	0.15 parts by mass

(Example 7)

The composition of Example 7 was prepared in the same manner as in Example 6 except for changing Binder Solution C to Binder Solution B in Example 6.

(Example 8)

The composition of Example 8 was prepared in the same manner as in Example 7 except for changing Inorganic Filler Liquid Dispersion 2 to Inorganic Filler Liquid Dispersion 4 in Example 7.

(Comparative Example 1)

The composition of Comparative Example 1 was prepared in the same manner as in Example 1 except for changing Binder Solution A to Binder Solution D and changing Inorganic Filler Liquid Dispersion 1 to Inorganic Filler Liquid Dispersion 3 in Example 1.

(Comparative Example 2)

The composition of Comparative Example 2 was prepared in the same manner as in Example 1 except for removing YMF-02 (a liquid dispersion of cesium tungsten oxide) in Example 1.

(Comparative Example 3)

The composition of Comparative Example 3 was prepared according to the same formulation as in Example 1 except for changing YMF-02 (a liquid dispersion of cesium tungsten oxide) to Carbon Black Liquid Dispersion A below.

(Preparation of Carbon Black Liquid Dispersion A)

Composition I below was subjected to a high-viscosity dispersion treatment by a twin-roll process to obtain a dispersion. At this time, the viscosity of the dispersion was 70,000 mPa·s.

Thereafter, a mixture of Composition II below was added to the dispersion obtained above, and the resulting mixture was stirred for 3 hours by using a homogenizer under the condition of 3,000 rpm. The mixed solution obtained was subjected to a fine dispersion treatment for 4 hours in a disperser (DISPERMAT, trade name, manufactured by GETZMANN GmbH) using zirconia beads of 0.3 mm in diameter to prepare Carbon Black Liquid Dispersion A.

(Composition I)

Carbon black with an average primary particle diameter of 23 nm (Pigment Black 7)

A propylene glycol monomethyl ether acetate 22 parts by mass
45 mass% solution of benzyl
methacrylate/methacrylic acid copolymer
(benzyl methacrylate unit/methacrylic acid unit
= 67/33 (mol%), Mw: 28,000)
Solsperse 5000 (produce by Lubrizol Japan 1.2 parts by mass
Ltd.)

(Composition II)

A propylene glycol monomethyl ether acetate 22 parts by mass
45 mass% solution of benzyl
methacrylate/methacrylic acid copolymer
(benzyl methacrylate unit/methacrylic acid unit
= 67/33 (mol%), Mw: 28,000)
Propylene glycol monomethyl ether acetate 200 parts by mass

<Evaluation of Polymerizable Composition>

(Evaluation of Step Followability)

An uneven substrate was produced by providing lines having a height of 20 μm (corresponding to the thickness of wiring 502 in Fig. 11) and a width or gap of 50 μm (corresponding to the wiring-to-wiring distance W in Fig. 11) on a silicon substrate, and each of the polymerizable compositions of Examples and Comparative Examples was coated on the uneven substrate by a spin coating method under the conditions of forming a film having a thickness of 10 μm on a flat silicon substrate, then heated (pre-baked) at 100°C for 120 seconds and further UV-cured by a UV exposure machine, ML-501C/B, manufactured by Ushio Inc. The cross-sectional SEM of the uneven portion was photographed, and the film thickness in the thinnest part of the concave portion (corresponding to the inter-wiring region C in Fig. 11) was measured to evaluate the step followability. Assuming that the target thickness of 10 μm is 100, the film thickness in the thinnest part was evaluated by the relative value. A relative value closer to 100 indicates that the step followability is higher and the shape of the photosensitive layer more successfully follows the uneven shape of the substrate.

(Formation of Resist Pattern and Evaluation of Sensitivity)

Each of the polymerizable compositions of Examples and Comparative Examples was coated on a silicon wafer by a spin coating method to give a film thickness of 25 μm and then heated on a hot plate at 120°C for 2 minutes to obtain a photosensitive layer.

The obtained photosensitive layer was irradiated by using an i-line stepper through a photomask having a square pattern with one side of 100 μm while changing the exposure dose in steps of 50 mJ/cm^2 in the range of 50 to 2,000 mJ/cm^2 .

The photosensitive layer after the exposure above was subjected to puddle development at 25°C for 40 seconds by using an aqueous 2.38 mass% tetramethylammonium hydroxide solution, then rinsed by spin shower and further washed with pure water to obtain an infrared-blocking solder resist pattern. The minimum exposure dose (sensitivity) for obtaining a square pattern with one side of 100 μm when performing the development step for 60 seconds was measured and used as an indication of pattern formability. As the numerical value is smaller, the sensitivity is judged as higher.

(Evaluation of Infrared-Blocking Effect and Visible Light Transparency)

The polymerizable composition was spin-coated on a glass substrate under the above-described conditions to form a photosensitive layer (polymerizable composition layer) coating having a film thickness of 25 μm , and the transmittance at a wavelength of 1,200 nm of the coating was measured using Ultraviolet-Visible-Near Infrared Spectrophotometer UV3600 (manufactured by Shimadzu Corporation). As the numerical value is smaller, the infrared-blocking effect is judged as higher. When the transmittance is 2% or less, the coating can be said to exhibit a practically good infrared-blocking effect.

Furthermore, the transmittance at a wavelength of 550 nm of the coating above was measured using Ultraviolet-Visible-Near Infrared Spectrophotometer UV3600 (manufactured by Shimadzu Corporation). As the numerical value is larger, the visible light transparency is judged as higher. When the transmittance of visible light is 30% or more, the coating can be said to exhibit a practically good visible light transparency.

(Evaluation of Resolution)

Exposure and development treatment were performed at the minimum exposure dose (sensitivity) calculated in the evaluation of sensitivity under the same conditions as in the formation of resist pattern by using a photomask having a 1:1 line-and-space pattern with a

line width of 100 μm to obtain a resist pattern of 1:1 line-and-space pattern having a line width of 100 μm . The linearity of the formed pattern was observed using an electron microscope (S-4800, manufactured by Hitachi High-Technologies Corporation) and ranked according to the following ratings.

Rank 5: The linearity of pattern is good, and the cross-section is rectangular and in a good level.

Rank 4: The linearity of pattern is substantially good, and the cross-section is substantially rectangular and in a level of no problem.

Rank 3: The linearity of pattern and the rectangularity of cross-section are slightly bad but in a level of practically no problem.

Rank 2: The linearity of pattern is significantly bad and the cross-section is off-rectangular.

Rank 1: Both the linearity of pattern and the rectangularity of cross-section are apparently bad.

The results of the evaluations above are shown in the Table below.

Table 1

	Infrared-Blocking Effect (1200 nm)	Visible Light Transparency (550 nm)	Sensitivity (mJ/cm^2)	Step Follow-ability	Resolution
Example 1	<1%	53%	450	150	3
Example 2	<1%	52%	450	140	3
Example 3	<1%	52%	400	130	4
Example 4	<1%	52%	350	125	4
Example 5	<1%	52%	400	130	4
Example 6	<1%	52%	400	110	5
Example 7	<1%	52%	300	105	5
Example 8	<1%	52%	300	100	5
Comparative Example 1	<1%	53%	The pattern could not be resolved.	150	—
Comparative Example 2	21%	75%	200	125	5
Comparative Example 3	<1%	<1%	The pattern could not be resolved.	170	—

As seen from the results in Table 1, according to the polymerizable composition of

the present invention, a pattern satisfying all of the requirements, that is, (1) the light-blocking effect in the infrared region is high, (2) the light transparency in the visible region is high, and (3) the resolution by alkali development is high, could be formed. Also, it is seen that a photosensitive layer having a shape successfully following the uneven shape of an uneven substrate could be formed.

On the other hand, in Comparative Examples 1 and 3, the pattern could not be resolved. Therefore, the sensitivity and resolution could not be evaluated on the compositions of Comparative Examples 1 and 3. In Comparative Example 2, the light-blocking effect in the infrared region was not obtained.

Industrial Applicability

According to the present invention, a polymerizable composition exhibiting high light-blocking effect in the infrared region and high light transparency in the visible region and being capable of forming a pattern with excellent resolution by alkali development, and a photosensitive layer, a permanent pattern, a wafer-level lens, a solid-state imaging device and a pattern forming method, each using the composition, can be provided.

Furthermore, according to the present invention, a polymerizable composition ensuring that when the substrate on which a photosensitive layer is provided has an uneven shape, a photosensitive layer having a shape successfully following the uneven shape of the substrate can be formed, and a photosensitive layer, a permanent pattern, a wafer-level lens, a solid-state imaging device and a pattern forming method, each using the composition, can be provided.

This application is based on a Japanese patent application filed on November 30, 2010 (Japanese Patent Application No. 2010-267889), and the contents thereof are incorporated herein by reference.

[Reference Signs List]

- 10 Silicon substrate
- 12 Imaging device
- 13 Interlayer insulating film
- 14 Base layer
- 15 Color filter

16	Overcoat
17	Microlens
18	Light-shielding film
20	Adhesive
22	Insulating film
23	Metal electrode
24	Solder resist layer
26	Internal electrode
27	Device surface electrode
30	Glass substrate
40	Imaging lens
41	Adhesive
42	Infrared cut filter
43	Adhesive
44	Light-blocking and electromagnetic shield
45	Adhesive
50	Lens holder
60	Solder ball
70	Circuit substrate
100	Solid-state imaging device substrate
200	Camera module
410	Substrate
412, 420	Lens
412a	Lens surface
412b	Lens edge
414	Light-shielding film
414A	Light-shielding coating layer
414a	Lens opening
450	Dispenser
460, 480	Mold
462, 482	Concave
470	Mask
501	Silicon substrate

502 Wiring
503 Photosensitive layer
C Inter-wiring region

95
CLAIMS

1. A polymerizable composition comprising:
a polymerization initiator,
a polymerizable compound,
a tungsten compound,
an alkali-soluble binder, and
an inorganic filler.
2. The polymerizable composition as claimed in claim 1, wherein the inorganic filler is silica.
3. The polymerizable composition as claimed in claim 1 or 2, wherein the alkali-soluble binder has an acid group.
4. The polymerizable composition as claimed in any one of claims 1 to 3, wherein the acid group is a phenolic hydroxyl group or a thiol group.
5. The polymerizable composition as claimed in any one of claims 1 to 4, wherein the alkali-soluble binder has a crosslinking group.
6. The polymerizable composition as claimed in any one of claims 1 to 5, wherein the polymerization initiator is an acetophenone-based compound and the polymerizable composition further contains a sensitizer.
7. The polymerizable composition as claimed in any one of claims 1 to 6, wherein the tungsten compound is represented by the following formula (I):



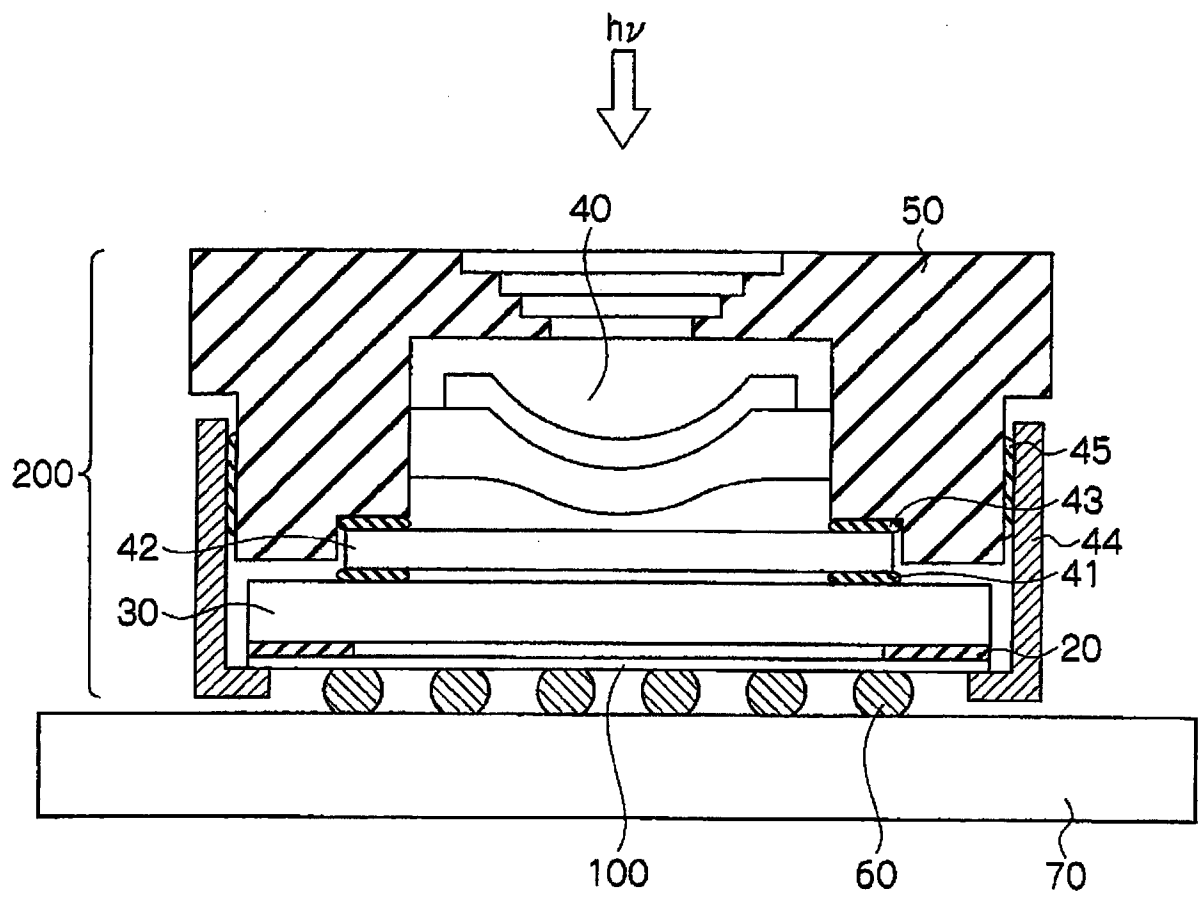
wherein M represents a metal, W represents tungsten, O represents oxygen,
 $0.001 \leq x/y \leq 1.1$, and
 $2.2 \leq z/y \leq 3.0$.

8. The polymerizable composition as claimed in claim 7, wherein M is an alkali metal.
9. The polymerizable composition as claimed in any one of claims 1 to 8, wherein the polymerizable compound is a polyfunctional polymerizable compound having a plurality of polymerizable groups within the molecule.
10. The polymerizable composition as claimed in any one of claims 1 to 9, which is used for a solder resist.
11. A photosensitive layer formed of the polymerizable composition claimed in any one of claims 1 to 10.
12. A permanent pattern formed of the polymerizable composition claimed in any one of claims 1 to 10.
13. The permanent pattern as claimed in claim 12, wherein the permanent pattern is a solder resist layer.
14. The permanent pattern as claimed in claim 12, wherein the permanent pattern is an infrared-blocking film.
15. A wafer-level lens having a lens and the permanent pattern claimed in claim 12 formed in the circumferential edge part of the lens.
16. A solid-state imaging device having the permanent pattern claimed in any one of claims 12 to 15.
17. A solid-state imaging device comprising:
 - a solid-state imaging device substrate having formed on one surface thereof an imaging element part, and
 - an infrared-blocking film provided on the other surface side of the solid-state imaging device substrate,wherein the infrared-blocking film is the permanent pattern claimed in claim 12.

18. A pattern forming method comprising, in order, a step of forming the photosensitive layer claimed in claim 11, a step of patternwise exposing said photosensitive layer to cure the exposed area, and a step of removing the unexposed area by alkali development to form a permanent pattern.

1/7

FIG. 1



2/7

FIG. 2

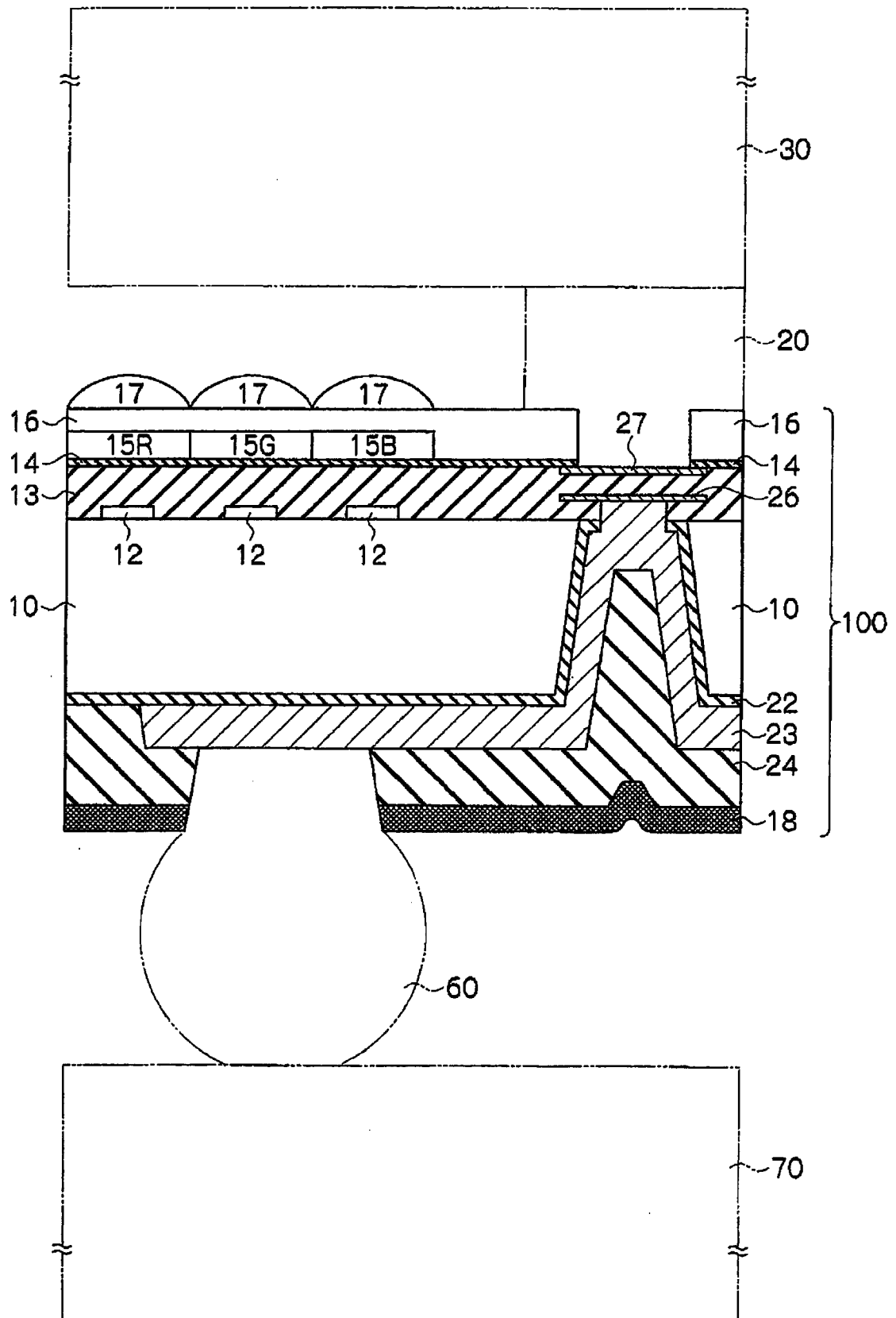


FIG. 3

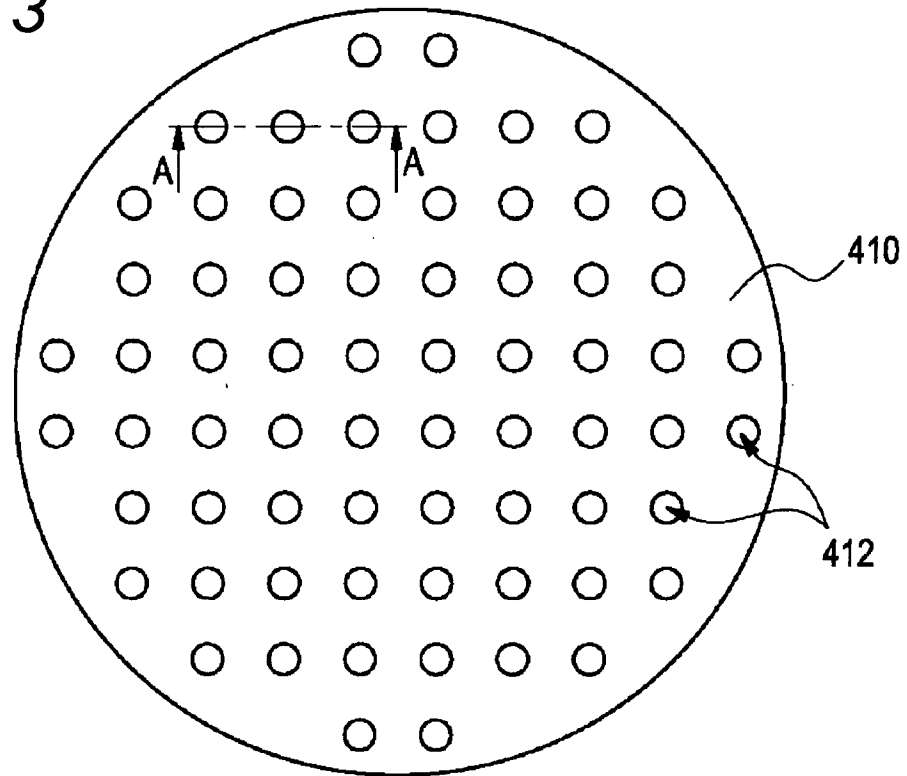


FIG. 4

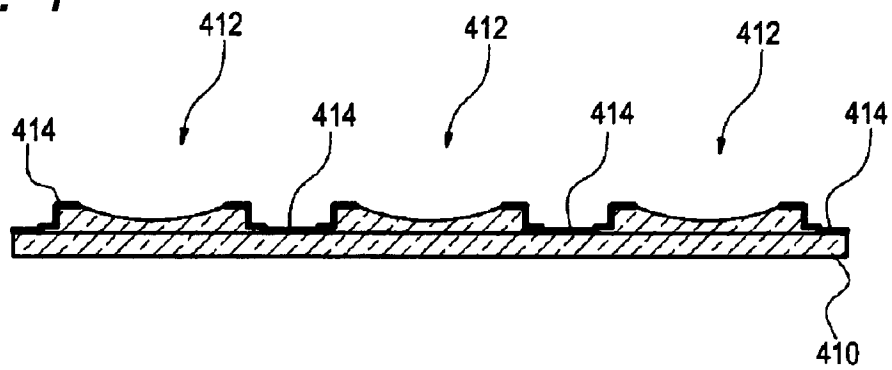


FIG. 5

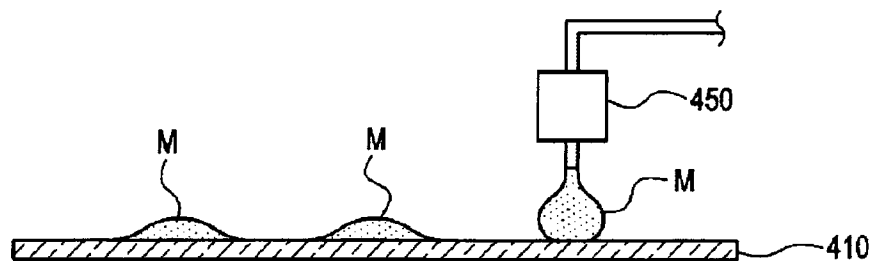


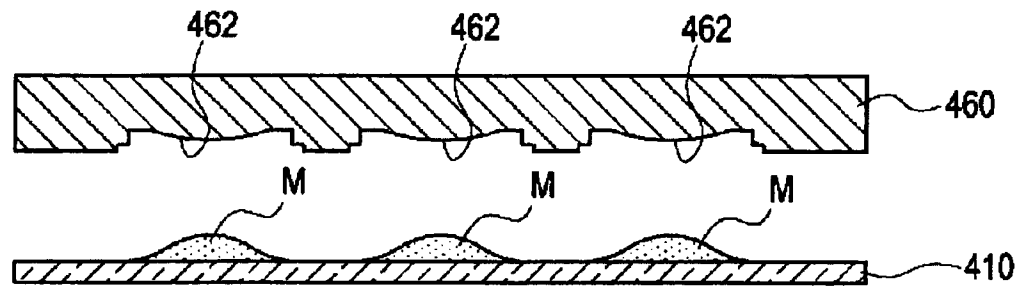
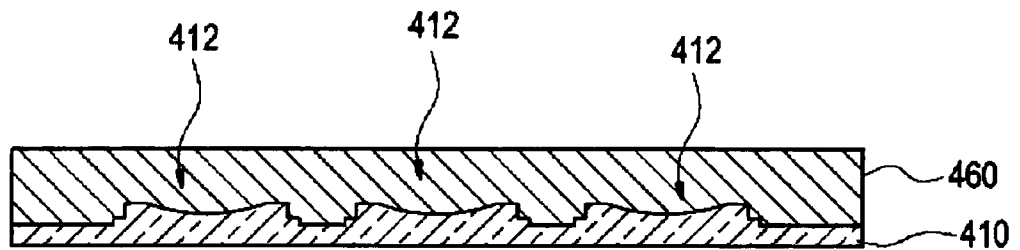
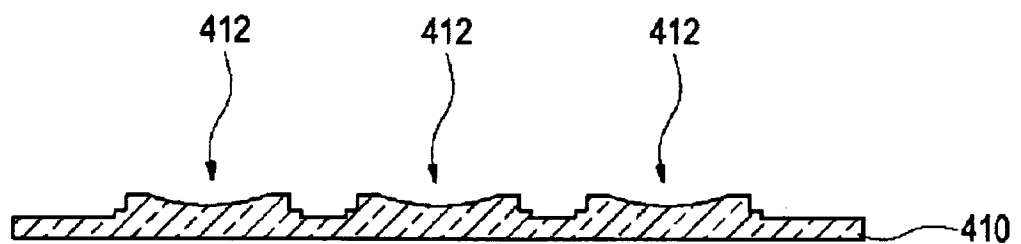
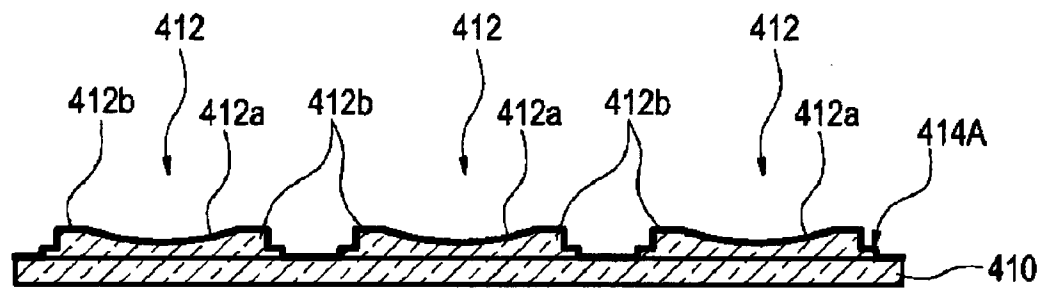
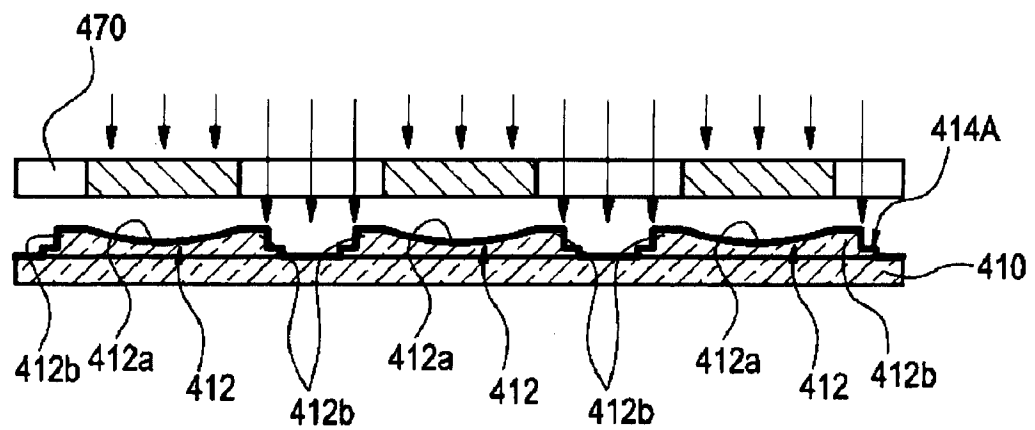
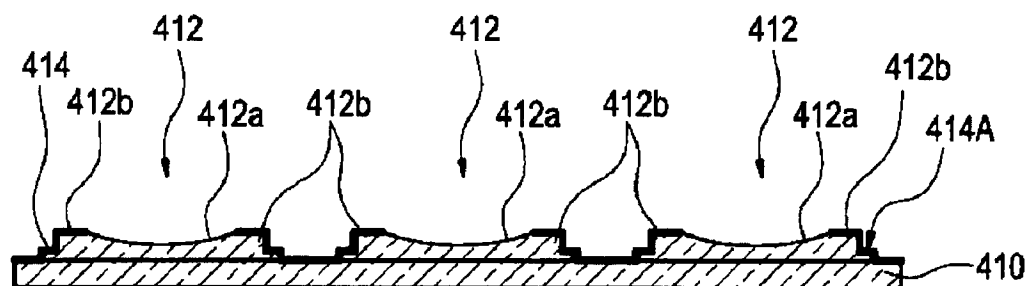
FIG. 6A*FIG. 6B**FIG. 6C*

FIG. 7A*FIG. 7B**FIG. 7C*

6/7

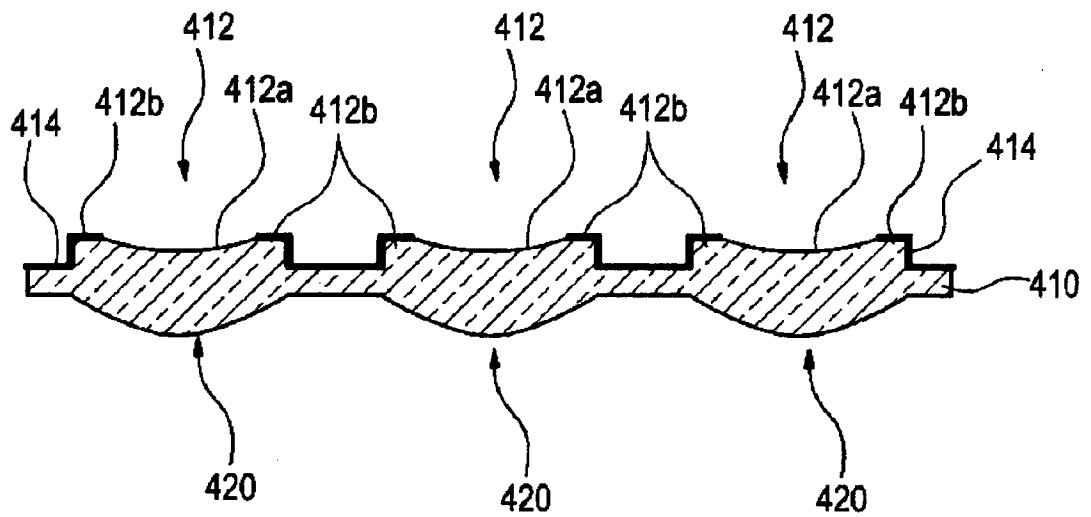
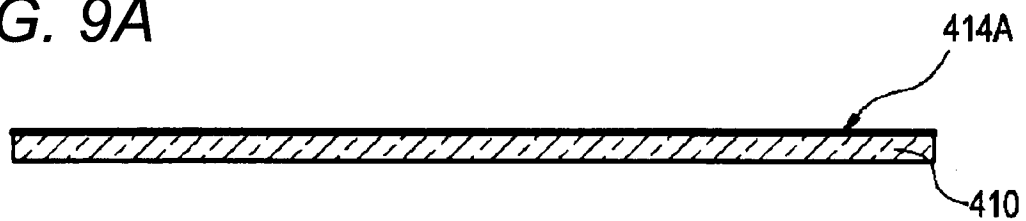
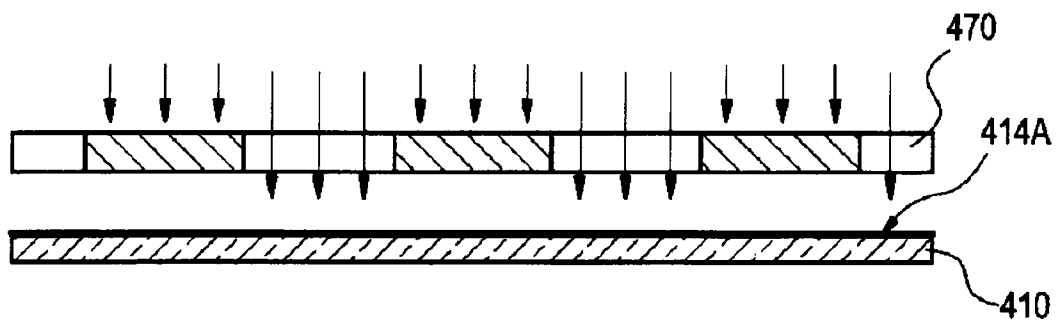
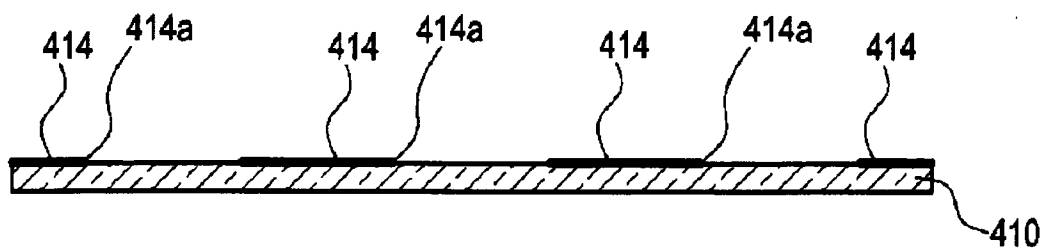
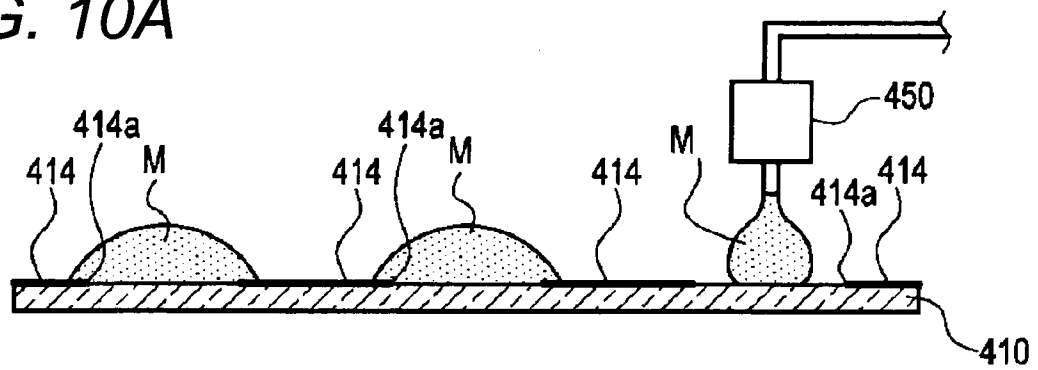
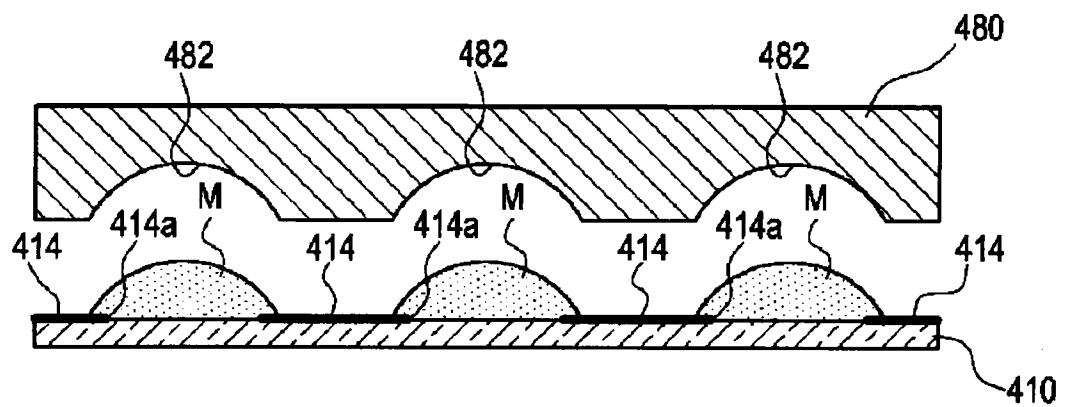
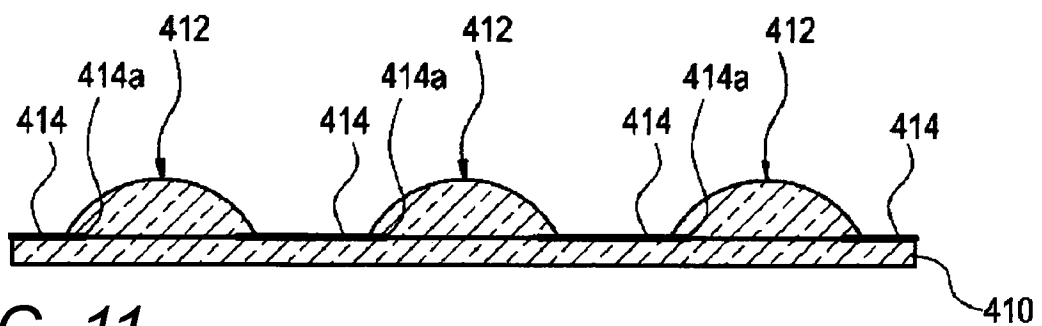
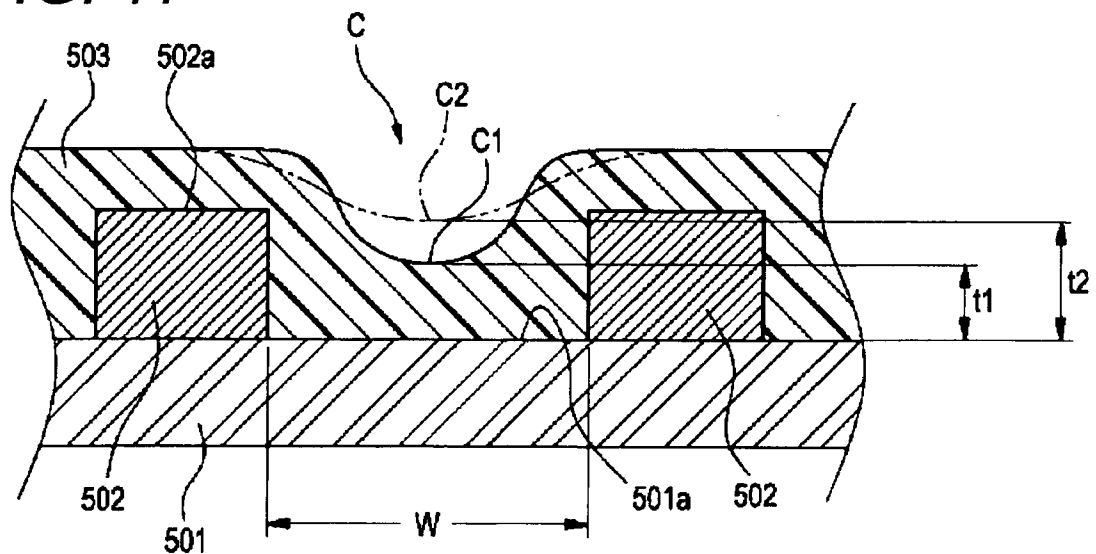
FIG. 8**FIG. 9A****FIG. 9B****FIG. 9C**

FIG. 10A**FIG. 10B****FIG. 10C****FIG. 11**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/078230

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. G03F7/004 (2006.01) i, G03F7/031 (2006.01) i, G03F7/038 (2006.01) i,
H05K3/28 (2006.01) i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. G03F7/004, G03F7/031, G03F7/038, H05K3/28

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2011
Registered utility model specifications of Japan 1996-2011
Published registered utility model applications of Japan 1994-2011

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2007-147854 A (MITSUBISHI PAPER MILLS LTD) 2007.06.14, (no family)	1-18
A	JP 63-216042 A (HITACHI LTD) 1988.09.08, & US 5061599 A & JP 2516207 B2	1-18
A	JP 10-265270 A (TORAY IND INC) 1998.10.06, (no family)	1-18

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

☐ See patent family annex.

* Special categories of cited documents:

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“&” document member of the same patent family

Date of the actual completion of the international search

27.12.2011

Date of mailing of the international search report

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