



(51) International Patent Classification:

C08L 101/02 (2006.01) **G02B 1/04** (2006.01)
C08F 2/44 (2006.01) **G03F 7/004** (2006.01)
C08F 2/48 (2006.01) **G03F 7/031** (2006.01)
C08J 3/09 (2006.01) **H01L 27/14** (2006.01)
C08K 3/22 (2006.01)

(21) International Application Number:

PCT/JP2012/063402

(22) International Filing Date:

18 May 2012 (18.05.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2011-111735 18 May 2011 (18.05.2011) JP

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(81) Designated States (*unless otherwise indicated, for every*

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every*

kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) Title: DISPERSION COMPOSITION, CURABLE COMPOSITION, TRANSPARENT FILM, MICROLENS AND SOLID-STATE IMAGE SENSING DEVICE USING THE SAME, METHOD FOR MANUFACTURING TRANSPARENT FILM, METHOD FOR MANUFACTURING MICROLENS AND METHOD FOR MANUFACTURING SOLID-STATE IMAGE SENSING DEVICE

(57) Abstract: A dispersion composition includes: colorless or transparent metal oxide particles (A) having a primary particle diameter of from 1 nm to 100 nm; a resin (B1) which has a repeating unit having a group X having a functional group with a pKa of 14 or less, and has an oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000 in a side chain thereof, and which also contains a basic nitrogen atom; and a solvent (C).



DESCRIPTION

Title of Invention

DISPERSION COMPOSITION, CURABLE COMPOSITION, TRANSPARENT FILM,
MICROLENS AND SOLID-STATE IMAGE SENSING DEVICE USING THE SAME,
METHOD FOR MANUFACTURING TRANSPARENT FILM, METHOD FOR
MANUFACTURING MICROLENS AND METHOD FOR MANUFACTURING
SOLID-STATE IMAGE SENSING DEVICE

Technical Field

The present invention relates to a dispersion composition, a curable composition, a transparent film, a microlens and a solid-state image sensing device using the same, a method for manufacturing a transparent film, a method for manufacturing a microlens and a method for manufacturing a solid-state image sensing device.

Background Art

As a use of optical interconnection which replaces a microlens or copper interconnection used in the imaging optics of a on-chip color filter such as an electronic copy machine and a solid-state image sensing device, a composition for forming a transparent member is required, which has a high refractive index, and which is able to form a micro transparent film, a transparent interconnection and the like.

In particular, a microlens used in a solid-state image sensing device is required to be more miniaturized as the miniaturization of the solid-state image sensing device progresses, and to have a high refractive index in order to achieve more effective light focusing. For example, a photopolymerizable composition capable of forming a high refractive index pattern, using silica-coated titanium oxide particles, is disclosed (see, for example, Japanese Patent Application Laid-Open No. 2009-179678). A composition for a solid-state image sensing device using a metal oxide which has 20% or more of silicon atoms on the particle surface is disclosed, and thus, it is described that the high refractive index and excellent pattern forming property are obtained (see, for example, Japanese Patent Application Laid-Open No. 2008-185683). In particular, recently, as a resolution becomes higher, the size of a pixel is correspondingly reduced, and thus, it is essential to collect light more efficiently. Accordingly, a microlens having a higher refractive index is required. In order to create

more devices in one manufacturing process, the size of a wafer used is increasing.

However, if the wafer size increases, a film formed in order to obtain a microlens has a problem in that a variation of performances may occur in a plurality of solid-state image sensing device chips obtained by being cut from the wafer since the difference in film thickness between the center portion and the peripheral portion of the wafer increases.

Summary of Invention

The present invention has been made in consideration of the above-described situations, and an object of the present invention is to provide a dispersion composition which has excellent dispersibility and dispersion stability, and also which has a high refractive index and light transmittance when prepared as a curable composition, which is able to form a film having a small difference in film thickness between the center portion and the peripheral portion thereof even when the composition is applied on a large size wafer, and a curable composition, a transparent film, a microlens and a solid-state image sensing device using the same, a method for manufacturing a transparent film, a method for manufacturing a microlens and a method for manufacturing a solid-state image sensing device.

Meanwhile, although a resin for dispersing a black color material being able to form a light-shielding film for a solid-state image sensing device which has a high-molecular weight oligomer chain or polymer chain in a side chain thereof and also contains a nitrogen atom, is known (see Japanese Patent Application Laid-Open No. 2010-6932), there is no description, in particular, about a dispersion composition having a high refractive index and light transmittance, which is able to form a film having a small difference in the film thickness.

Specific means in order to solve the problem are as follows.

<1> A dispersion composition, comprising:

colorless or transparent metal oxide particles (A) having a primary particle diameter of from 1 nm to 100 nm;

a resin (B1) which has a repeating unit having a group X having a functional group with a pKa of 14 or less, and has an oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000 in a side chain thereof, and which also contains a basic nitrogen atom; and

a solvent (C).

<2> The dispersion composition as described in <1> above, wherein the resin (B1) is a resin (B2) which has a repeating unit containing a nitrogen atom bonded to the group X

having a functional group with a pKa of 14 or less, and an oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000 in a side chain thereof.

<3> The dispersion composition as described in <1> or <2> above, wherein the dispersion composition comprises:

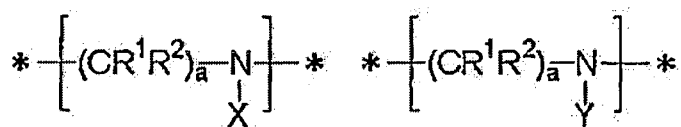
colorless or transparent metal oxide particles (A) having a primary particle diameter of from 1 nm to 100 nm,

a resin (B) having (i) at least one repeating unit containing a nitrogen atom, selected from a poly(lower alkyleneimine)-based repeating unit, a polyallylamine-based repeating unit, a polydiallylamine-based repeating unit, a metaxylenediamine-epichlorohydrin polycondensate-based repeating unit and a polyvinylamine-based repeating unit, wherein the repeating unit has a group X that has a functional group with a pKa of 14 or less and the group X is bonded to the nitrogen atom, and (ii) an oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000 in the side chain thereof, and

a solvent (C).

<4> The dispersion composition as described in any one of <1> to <3> above, wherein the functional group with a pKa of 14 or less which the group X has is carboxylic acid, sulfonic acid or $-\text{COCH}_2\text{CO}-$.

<5> The dispersion composition as described in <3> or <4> above, wherein the resin (B) is a resin comprising a repeating unit represented by the following general formula (I-1) and a repeating unit represented by the general formula (I-2):



Formula(I-1)

Formula(I-2)

in the general formula (I-1) and the general formula (I-2),

each of R^1 and R^2 independently represents a hydrogen atom, a halogen atom or an alkyl group,

each of a's independently represents an integer of from 1 to 5,

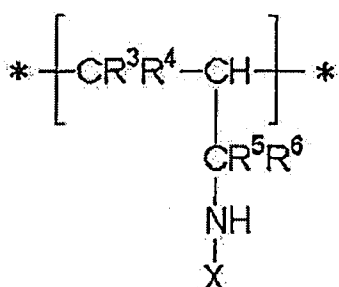
* represents a linking portion between the repeating units,

X represents a group having a functional group having a pKa of 14 or less,

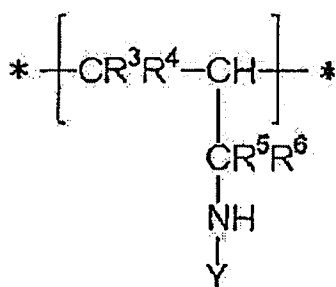
Y represents an oligomer chain or polymer chain having the number of atoms of from

40 to 10,000.

<6> The dispersion composition as described in <3> or <4> above, wherein the resin (B) is a resin containing a repeating unit represented by the following general formula (II-1) and a repeating unit represented by the general formula (II-2):



Formula(II-1)



Formula(II-2)

in the general formula (II-1) and the general formula (II-2),
each of R^3 , R^4 , R^5 and R^6 independently represents a hydrogen atom, a halogen atom or an alkyl group,

* represents a linking portion between the repeating units,

X represents a group having a functional group having a pKa of 14 or less,

Y represents an oligomer chain or polymer chain having the number of atoms of from 40 to 10,000.

<7> The dispersion composition as described in any one of <1> to <6> above, wherein the oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000 has a structure represented by the following formula (III-1):



Formula(III-1)

in the general formula (III-1), Z is a polymer or oligomer having a polyester chain as a partial structure, and represents a residue except the carboxyl group from a polyester having a free carboxylic acid represented by the following general formula (IV):



Formula(IV)

in the general formula (IV), Z is the same as Z in the general formula (III-1).

<8> A curable composition, comprising:

the dispersion composition as described in any one of <1> to <7> above,

wherein the dispersion composition further contains a polymerizable compound (D) and a polymerization initiator (E).

<9> The curable composition as described in <8> above, further comprising:
a binder polymer.

<10> The curable composition as described in <8> or <9> above,
wherein the polymerization initiator (E) is an oxime-based polymerization initiator.

<11> The curable composition as described in any one of <8> to <10> above, which
is used for forming a microlens.

<12> A transparent film, which is formed by using the curable composition as
described in any one of <8> to <11> above.

<13> A microlens, which is formed by using the transparent film as described in
<12> above.

<14> A solid-state image sensing device comprising:
the microlens as described in <13> above.

<15> A method for manufacturing a transparent film, comprising:
a process of applying the curable composition as described in any one of <8> to <10>
above on a wafer,

a subsequent first heating process of heating the composition, and

a subsequent second heating process of heating the composition at a temperature
higher than the temperature in the first heating process.

<16> A method for manufacturing a microlens, comprising:
a process of subjecting the transparent film as described in <12> above to post bake
treatment to shape the transparent film, and
a process of dry etching the transparent film.

<17> A method for manufacturing a solid-state image sensing device, comprising:
a process of forming red pixels, blue pixels, and green pixels on a substrate for a
solid-state image sensing device having at least a photodiode, a light-shielding film, and a

device protective film,

a process of applying the curable composition as described in any one of <8> to <10> above and performing heating,

a process of forming a resist pattern,

a process of shaping the formed resist pattern into a lens-type shape by performing post-bake treatment, and

a process of performing dry etching.

In the dispersion composition in the present invention, as described in detail below, the metal oxide particles (A) interact with both the nitrogen atom and the functional group with a pKa of 14 or less which the group X has in the resin (B1), and also the resin (B1) has an oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000, thereby for example, the oligomer chain or polymer chain Y may function as a sterically repulsive group to exhibit excellent dispersibility, thereby uniformly dispersing metal oxide particles as high refractive index particles. Even when the dispersion composition is stored at room temperature and the like for a long period of time, the oligomer chain or polymer chain Y interacts with a solvent, thereby precipitation of the metal oxide particles can be inhibited for a long period of time. Moreover, when a coating film is formed by the dispersion composition (more specifically, for example, a curable composition), the oligomer chain or polymer chain Y functions as a sterically repulsive group to prevent metal oxide particles from aggregating, and thus, the dispersibility and the dispersion stability are not easily impaired as described above even though the content of metal oxide particles is increased. That is, the dispersion composition of the present invention may be used to achieve excellent dispersibility and dispersion stability and obtain a film having a very high refractive index.

When the resin (B1) is used to compose a dispersion composition and the dispersion composition is used to constitute a curable dispersion, the uniformity of the film thickness in a coating film obtained by the curable composition is excellent, and as a result, even when the composition is applied on a large size wafer, a film having a small difference in film thickness between the center portion and the peripheral portion of the wafer (for example, a film for forming a microlens and the like) may be obtained. It is presumed that this is because the oligomer chain or polymer chain Y of the resin (B1) of the present invention and the solvent exhibit excellent interaction with each other, for example, in the coating film.

According to the present invention, it is possible to provide a dispersion composition having excellent dispersibility and dispersion stability, and having a high refractive index and light transmittance when prepared as a curable composition, which is able to form a film having a small difference in film thickness between the center portion and the peripheral portion thereof even when the composition is applied on a large size wafer, and a curable composition, a transparent film, a microlens and a solid-state image sensing device using the same, a method for manufacturing a transparent film, a method for manufacturing a microlens and a method for manufacturing a solid-state image sensing device.

Description of Embodiments

Hereinafter, the dispersion composition of the present invention will be described in detail.

Meanwhile, in representation of a group (atomic group) in the present specification, any expression which does not describe substitution and unsubstitution includes one having substituent groups as well as one having no substituent groups. For example, “an alkyl group” includes an alkyl group having no substituent groups (unsubstituted alkyl group) as well as an alkyl group having substituent groups (substituted alkyl group).

The explanation of constituent elements described hereinafter may be made based on the representative exemplary embodiment of the present invention, but the present invention is not limited to such an exemplary embodiment. Herein, in the present specification, a numerical range represented by using “to” denotes a range including numerical values described before and after “to” as a lower limit and an upper limit.

Herein, in the present specification, “(meth)acrylate” represents acrylate and methacrylate, “(meth)acryl” represents acryl and methacryl, and “meth(acryloyl)” represents acryloyl and methacryloyl. In the present specification, “monomeric body” and “monomer” are the same as each other. In the present invention, monomer is differentiated from oligomer and polymer, and the monomer refers to a compound having a mass average molecular weight of 2,000 or less. In the present specification, a polymerizable compound refers to a compound having a polymerizable group(s), and may be a monomer or a polymer. The polymerizable group refers to a group which is involved in a polymerization reaction.

In the present invention, “refractive index”, unless otherwise specified, refers to a refractive index with respect to light having a wavelength of 500 nm.

<Dispersion Composition>

A dispersion composition of the present invention contains colorless or transparent metal oxide particles (A) having a primary particle diameter of from 1 nm to 100 nm, a resin (B1) which has a repeating unit having a group X having a functional group with a pKa of 14 or less, and an oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000 in the side chain thereof (in the side chain of the resin or the repeating unit) and which also contains a basic nitrogen atom, and a solvent (C).

It is particularly preferred that the dispersion composition of the present invention contains colorless or transparent metal oxide particles (A) having a primary particle diameter of from 1 nm to 100 nm, a resin (B) including (i) at least one repeating unit containing a nitrogen atom, selected from a poly(lower alkyleneimine)-based repeating unit, a polyallylamine-based repeating unit, a polydiallylamine-based repeating unit, a metaxylenediamine-epichlorohydrin polycondensate-based repeating unit and a polyvinylamine-based repeating unit, wherein the repeating unit has a group X that has a functional group with a pKa of 14 or less and the group X is bonded to the nitrogen atom, and (ii) an oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000 in the side chain thereof, and a solvent (C).

Due to having the configuration, it is possible to provide a dispersion composition having excellent dispersibility and dispersion stability, and also having a very high refractive index when prepared as a curable dispersion as described below, which is able to form a film having a small difference in film thickness between the center portion and the peripheral portion thereof (representatively, a transparent film) even when the composition is applied on a large size wafer.

<(A) Colorless or transparent metal oxide particles having primary particle diameter of from 1 nm to 100 nm>

In the present invention, the colorless or transparent metal oxide particles (A) are colorless or transparent inorganic particles having a high refractive index, and examples thereof include oxide particles of titanium (Ti), zirconium (Zr), aluminum (Al), silicon (Si), zinc (Zn) or magnesium (Mg), preferably titanium dioxide (TiO₂) particles, zirconium dioxide (ZrO₂) particles or silicon dioxide (SiO₂) particles, and among them, titanium dioxide particles (hereinafter, simply referred to as "titanium dioxide" in some cases) is preferred.

In the present invention, the colorless or transparent titanium dioxide particles may be

represented by chemical formula TiO_2 , and have a purity of preferably 70% or more, more preferably 80% or more and even more preferably 85% or more. Lower order titanium oxide represented by the general formula $\text{Ti}_n\text{O}_{2n-1}$ (n represents a number of from 2 to 4), titanium oxynitride and the like are preferably 30 mass% or less, more preferably 20 mass% or less and even more preferably 15 mass% or less.

In the present invention, the metal oxide particles are not particularly limited as long as the particles have a primary particle diameter of from 1 nm to 100 nm, and for example, may be appropriately selected from commercially available metal oxide particles.

The metal oxide particles have a primary particle diameter of from 1 nm to 100 nm, preferably from 1 nm to 80 nm and particularly preferably from 1 nm to 50 nm. If the primary particle diameter of the metal oxide particles exceeds 100 nm, there are some cases where refractive index and transmittance may be reduced. When the diameter is less than 1 nm, there are some cases where dispersibility may be reduced by aggregation.

In the present invention, an average particle diameter may be used as an index of a primary particle diameter. In the present invention, the average particle diameter of metal oxide particles refers to a value obtained by performing measurement on a diluted solution obtained by diluting a mixed solution or a liquid dispersion including metal oxide particles to 80 times with propylene glycol monomethyl ether acetate using a dynamic light scattering method.

This measurement is calculated as a number average particle diameter obtained by performing measurement using MICROTRAC UPA-EX150 manufactured by NIKKISO Co., Ltd.

In the present invention, the refractive index of metal oxide particles is not particularly limited, but is preferably from 1.75 to 2.70 from the viewpoint of obtaining a high refractive index and more preferably 1.90 to 2.70.

The metal oxide particles have a specific surface area of preferably from $10 \text{ m}^2/\text{g}$ to $400 \text{ m}^2/\text{g}$, more preferably from $20 \text{ m}^2/\text{g}$ to $200 \text{ m}^2/\text{g}$, and most preferably from $30 \text{ m}^2/\text{g}$ to $150 \text{ m}^2/\text{g}$.

There is no particular limitation on the shape of metal oxide particles. For example, the shape may be a rice-grain shape, a spherical shape, a cubic shape, a spindle shape or an indefinite shape.

In the present invention, the metal oxide particles may be subjected to surface treatment with an organic compound(s). Examples of the organic compound used in the

surface treatment include polyol, alkanolamine, stearic acid, a silane coupling agent and a titanate coupling agent. Among them, the silane coupling agent is preferred.

The surface treatment may be performed either with one kind surface treatment agent alone or in combination of two or more surface treatment agents.

It is also preferred that the surface of the metal oxide particles is covered with oxides such as aluminum, silicon and zirconia. Thereby, the weather resistance is more enhanced.

As the metal oxide particles in the present invention, those commercially available products may be preferably used.

Examples of the commercially available products of the titanium dioxide particles include TTO series (TTO-51(A), TTO-51(C) and the like), TTO-S and V series (TTO-S-1, TTO-S-2, TTO-V-3 and the like) manufactured by ISHIHARA SANGYO KAISHA, LTD., MT series (MT-01, MT-05 and the like) manufactured by TAYCA CORP., and the like.

Examples of the commercially available products of the zirconium dioxide particles include UEP (manufactured by Daiichi Kigenso Kagaku Kogyo Ltd.), PCS (NIPPON DENKO CO., LTD.), JS-01, JS-03 and JS-04 (NIPPON DENKO CO., LTD.), UEP-100 (manufactured by Daiichi Kigenso Kagaku Kogyo Ltd.), and the like.

Examples of the commercially available products of the silicon dioxide particles include OG502-31 manufactured by Clariant Co., and the like.

In the present invention, the metal oxide particles may be used either alone or in combination of two or more thereof.

A content of the metal oxide particles in the dispersion composition of the present invention (or a curable composition as described below) is preferably from 10 mass% to 90 mass%, more preferably from 10 mass% to 50 mass%, even more preferably from 12 mass% and 40 mass% and particularly preferably from 15 mass% to 35 mass%, based on the total solid content of the dispersion composition from the viewpoint of dispersion stability (In this specification, mass ratio is equal to weight ratio.)

Meanwhile, particularly as a microlens having a high refractive index, the content is preferably from 50 mass% to 90 mass% and more preferably from 52 mass% to 85 mass%, based on the total solid content of the dispersion composition.

<Resin (B1) which has a repeating unit having a group X having functional group with pKa of 14 or less, and has an oligomer chain or polymer chain Y having number of atoms of from 40 to 10,000 in side chain thereof, and also contains a basic nitrogen atom>

Herein, the basic nitrogen atom is not particularly limited as long as the basic nitrogen

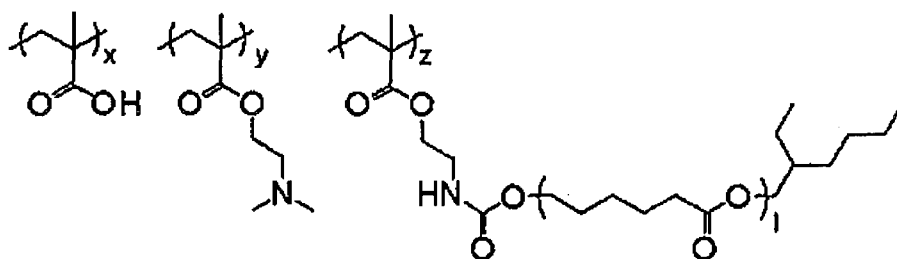
atom shows basicity, but the resin (B1) preferably contains a structure having a nitrogen atom with a pK_b of 14 or less and more preferably contains a structure having a nitrogen atom with a pK_b of 10 or less.

In the present invention, the base strength pK_b refers to a pK_b at a water temperature of 25°C, is one of the indices to quantitatively represent the intensity of a base, and is the same as the basicity constant. The base strength pK_b and an acid strength pK_a as described below have a relationship of $pK_b = 14 - pK_a$.

The group X having a functional group with a pK_a of 14 or less is the same as the group X as described below regarding the resin (B).

The oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000, which the resin (B1) has in the side chain thereof is also the same as the oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000 to be described below on the resin (B).

Examples of the resin (B1) include a resin containing a repeating unit which has a group X having a functional group with a pK_a of 14 or less represented by the following formula, a repeating unit having the basic nitrogen atom represented by the following formula, and a repeating unit which has an oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000, represented by the following formula (corresponding in sequence from the left side of a structure of the following repeating unit).



In the formula above, each of x, y and z represents a polymerization molar ratio of the repeating unit, and it is preferred that x is from 5 to 50, y is from 5 to 60, and z is from 10 to 90. 1 represents a connectivity number of a polyester chain, is an integer that may form an oligomer chain or polymer chain having the number of atoms of from 40 to 10,000, and is preferably from 70 to 2,000.

The resin (B1) is preferably a resin (B2) having a repeating unit which contains a nitrogen atom bonded to the group X having a functional group with a pK_a of 14 or less, and an oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000 in the

side chain thereof.

The resin (B1) is particularly preferably a resin (B) (hereinafter, suitably referred to "specific resin") having (i) at least one repeating unit containing a nitrogen atom, selected from a poly(lower alkyleneimine)-based repeating unit, a polyallylamine-based repeating unit, a polydiallylamine-based repeating unit, a metaxylenediamine-epichlorohydrin polycondensate-based repeating unit and a polyvinylamine-based repeating unit, wherein the repeating unit has a group X that has a functional group with a pKa of 14 or less and the group X is bonded to the nitrogen atom, and (ii) an oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000 in the side chain thereof.

((i) At least one repeating unit containing a nitrogen atom, selected from a poly(lower alkyleneimine)-based repeating unit, a polyallylamine-based repeating unit, a polydiallylamine-based repeating unit, a metaxylenediamine-epichlorohydrin polycondensate-based repeating unit and a polyvinylamine-based repeating unit)

In the present invention, the specific resin has (i) at least one repeating unit containing a nitrogen atom, selected from a poly(lower alkyleneimine)-based repeating unit, a polyallylamine repeating unit, a polydiallylamine-based repeating unit, a metaxylenediamine-epichlorohydrin polycondensate-based repeating unit, and a polyvinylamine-based repeating unit. Accordingly, the absorptive force to the surface of the metal oxide particles (A) is improved, and the interaction between the metal oxide particles may also be reduced.

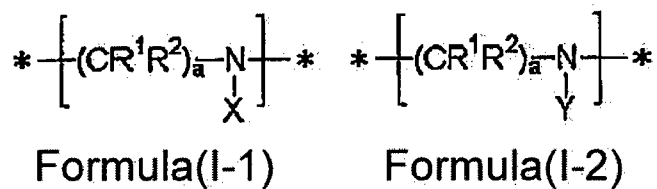
The poly(lower alkyleneimine) may be in a chain-shape or a mesh form.

The number average molecular weight of a main chain obtained by polymerizing at least one repeating unit (i) containing a nitrogen atom, selected from a poly(lower alkyleneimine)-based repeating unit, a polyallylamine-based repeating unit, a polydiallylamine-based repeating unit, a metaxylenediamine-epichlorohydrin polycondensate-based repeating unit, and a polyvinylamine-based repeating unit, that is, the number average molecular weight of a moiety except the oligomer chain or polymer chain Y moiety of the side chain from the resin (B) is preferably from 100 to 10,000, more preferably from 200 to 5,000, and most preferably from 300 to 2,000. The number average molecular weight of the main chain moiety may be determined from a proportion of the hydrogen atom integral value of the terminal group and of the main chain moiety measured by nuclear magnetic resonance spectroscopy or may be determined by the measurement of the molecular weight of the oligomer or polymer containing an amino group as a raw material.

The repeating unit (i) containing a nitrogen atom is particularly preferably a poly(lower alkyleneimine)-based repeating unit or a polyallylamine-based repeating unit. Meanwhile, in the present invention, the expression “lower” used in the poly(lower alkyleneimine) indicates that the number of carbon atoms is 1 to 5, and the lower-alkyleneimine represents an alkyleneimine having from 1 to 5 carbon atoms. If this structure is specified, it is preferred that the specific resin of the present invention includes a structure having a repeating unit represented by the general formula (I-1) and a repeating unit represented by the general formula (I-2) or a structure having a repeating unit represented by the general formula (II-1) and a repeating unit represented by the general formula (II-2).

(Repeating Unit Represented by General Formula (I-1) and Repeating Unit Represented by General Formula (I-2))

A repeating unit represented by the general formula (I-1) and a repeating unit represented by the general formula (I-2) as preferred constituting components of the specific resin of the present invention will be described in detail.



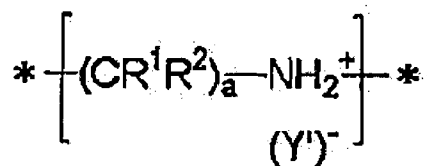
In the general formula (I-1) and the general formula (I-2),

each of R^1 and R^2 independently represents a hydrogen atom, a halogen atom, or an alkyl group. Each of a 's independently represents an integer of from 1 to 5. $*$ represents a linking portion between the repeating units.

X represents a group containing a functional group having a pK_a of 14 or less.

Y represents an oligomer chain or polymer chain having the number of atoms of from 40 to 10,000.

It is preferred that the specific resin of the present invention also has a repeating unit represented by the general formula (I-3) in addition to a repeating unit represented by the general formula (I-1) or the general formula (I-2), as a copolymerization component. When the resin is used as a dispersing agent of the metal oxide particles (A), the dispersion performance is further improved by using these repeating units in combination.



Formula(I-3)

In the general formula (I-3),

*, R^1 , R^2 and a are the same as in the general formula (I-1).

Y' represents an oligomer chain or polymer chain having an anion group, which has the number of atoms of from 40 to 10,000.

It is possible to form the repeating unit represented by the general formula (I-3) by performing a reaction by adding an oligomer or polymer having a group which reacts with an amine to form a salt to a resin having a primary or secondary amino group in the main chain moiety thereof. Here, as the anion group, CO_2^- or SO_3^- is preferable, and CO_2^- is most preferable. It is preferred that the anion group is present at the end of the oligomer chain or polymer chain which Y' has.

In the general formula (I-1), the general formula (I-2) and the general formula (I-3), R^1 and R^2 are particularly preferably a hydrogen atom. a is preferably 2 from the viewpoint of raw material availability.

The specific resin of the present invention may include lower alkyleneimine containing a primary or tertiary amino group as a repeating unit, in addition to the repeating units represented by the general formula (I-1), the general formula (I-2) and the general formula (I-3). The lower alkyleneimine represents an alkyleneimine having from 1 to 5 carbon atoms. The specific resin may or may not contain such a lower alkyleneimine repeating unit, but when the specific resin contains a lower alkyleneimine repeating unit, the lower alkyleneimine repeating unit is contained preferably in an amount of from 1 mol% to 60 mol% and most preferably in an amount of from 3 mol% to 40 mol%, based on the total repeating units included in the specific resin. Meanwhile, to the nitrogen atom in such a lower alkyleneimine repeating unit, the group represented by X , Y or Y' may also be bonded. A resin which includes both the repeating unit having a group represented by X bonded thereto and the repeating unit having Y bonded thereto in such a main chain structure is also encompassed in the specific resin of the present invention.

The repeating unit represented by the general formula (I-1) is a repeating unit containing a nitrogen atom to which a group X containing a functional group having a pK_a of

14 or less is bonded, and the repeating unit containing a nitrogen atom is contained preferably in an amount of from 1 mol% to 80 mol% and most preferably in an amount of from 3 mol% to 50 mol%, based on the total repeating units included in the resin of the present invention, from the viewpoint of storage stability and developability.

The repeating unit represented by the general formula (I-2) is a repeating unit which has an oligomer chain or polymer chain having the number of atoms of from 40 to 10,000, and the repeating unit is contained preferably in an amount of from 10 mol% to 90 mol%, and most preferably in an amount of from 30 mol% to 70 mol%, based on the total repeating units of the resin of the present invention, from the viewpoint of storage stability.

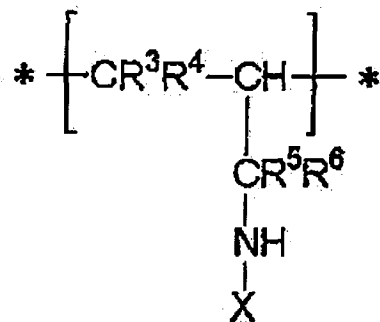
Upon reviewing the content ratios of both, the molar ratio of the repeating units (I-1):(I-2) is preferably in the range of from 10:1 to 1:100 and more preferably in the range of from 1:1 to 1:10, from the viewpoint of dispersion stability and balance of hydrophilicity and hydrophobicity.

Meanwhile, the repeating unit represented by the general formula (I-3), which is used in combination, as desired, is one in which a partial structure including an oligomer chain or polymer chain having the number of atoms of from 40 to 10,000 is ionically bonded to a nitrogen atom of the main chain, and is contained preferably in an amount of from 0.5 mol% to 20 mol% and most preferably in an amount of from 1 mol% to 10 mol%, based on the total repeating units of the resin of the present invention, from the viewpoint of the effect.

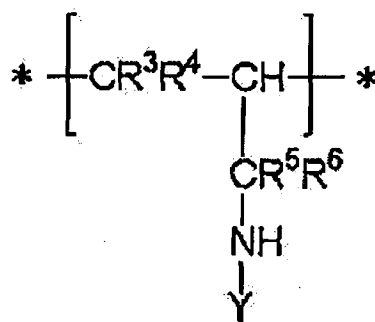
Meanwhile, the ionic bond of the polymer chain Y can be confirmed by infrared spectroscopy, or base titration.

(Repeating Unit Represented by General Formula (II-1) and Repeating Unit Represented by General Formula (II-2))

A repeating unit represented by the general formula (II-1) and a repeating unit represented by the general formula (II-2) as other preferred constituting components of the specific resin of the present invention will be described in detail.



Formula(II-1)

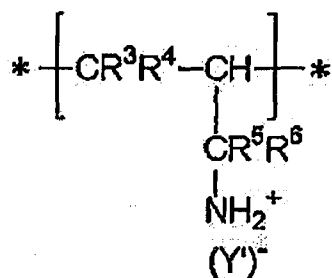


Formula(II-2)

In the general formula (II-1) and the general formula (II-2),

Each of R^3 , R^4 , R^5 and R^6 independently represents a hydrogen atom, a halogen atom and an alkyl group. *, X and Y are the same as *, X and Y in the general formula (I-1) and the general formula (I-2).

It is preferred that, in the present invention, the resin includes a repeating unit represented by the general formula (II-3) in addition to the repeating unit represented by the general formula (II-1) and the repeating unit represented by the general formula (II-2), as a copolymerization component. When the resin is used as a dispersing agent of the metal oxide particles (A), the dispersion performance is further improved by using these repeating units in combination.



Formula(II-3)

In the general formula (II-3), *, R^3 , R^4 , R^5 and R^6 are the same as in the general formula (II-1). Y' are the same as Y' in the general formula (I-3).

In the general formulas (II-1), (II-2) and (II-3), R^3 , R^4 , R^5 and R^6 are preferably a hydrogen atom from the viewpoint of raw material availability.

The general formula (II-1) is a repeating unit containing a nitrogen atom to which a group X containing a functional group having a pKa of 14 or less is bonded, and the repeating unit containing such a nitrogen atom is contained preferably in an amount of from 1 mol% to 80 mol% and most preferably in an amount of from 3 mol% to 50 mol%, based on the total repeating units included in the resin of the present invention, from the viewpoint of storage

stability and developability.

The general formula (II-2) is a repeating unit which has an oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000, and the repeating unit is contained preferably in an amount of from 10 mol% to 90 mol% and most preferably in an amount of from 30 mol% to 70 mol%, based on the total repeating units of the resin of the present invention, from the viewpoint of storage stability.

Upon reviewing the content ratios of both, the molar ratio of the repeating units (II-1):(II-2) is preferably in the range of from 10:1 to 1:100 and more preferably in the range of from 1:1 to 1:10, from the viewpoint of dispersion stability and balance of hydrophilicity and hydrophobicity.

The repeating unit represented by the general formula (II-3), which is used in combination, as desired, is contained preferably in an amount of from 0.5 mol% to 20 mol% and most preferably in an amount of from 1 mol% to 10 mol%, based on the total repeating units of the resin of the present invention.

In the specific resin of the present invention, it is most preferable to include both a repeating unit represented by the general formula (I-1) and a repeating unit represented by the general formula (I-2) from the viewpoint of dispersibility.

<Group X containing functional group having pKa of 14 or less>

X has a functional group having a pKa of 14 or less at a water temperature of 25°C. The "pKa" as mentioned herein is defined in Chemical Handbook (II) (4th Revised Edition, 1993, edited by The Chemical Society of Japan, Maruzen Co., Ltd.).

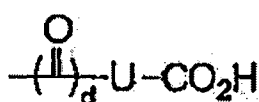
The "functional group having a pKa of 14 or less" is not particularly limited in structure and the like as long as the physical properties thereof satisfy this condition, and examples thereof include known functional groups having a pKa in the above-described range, but a functional group having a pKa of 12 or less is particularly preferred, and a group having a pKa of 11 or less is most preferred. Specifically, examples thereof include carboxylic acid (pKa is approximately from 3 to 5), sulfonic acid (pKa is approximately from -3 to -2), phosphonic acid (pKa is approximately from -1 to 4), -COCH₂CO- (pKa is approximately from 8 to 10), -COCH₂CN (pKa is approximately from 8 to 11), -CONHCO-, a phenolic hydroxyl group, -R_FCH₂OH or -(R_F)₂CHOH (R_F represents a perfluoroalkyl group. pKa is approximately from 9 to 11), a sulfonamide group (pKa is approximately from 9 to 11) and the like, and particularly preferably carboxylic acid (pKa is approximately from 3 to 5), sulfonic acid (pKa is approximately from -3 to -2), and -COCH₂CO- (pKa is approximately from 8 to

10).

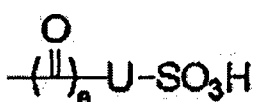
A pKa of the functional group which the group X has is 14 or less, and thus, an interaction with the metal oxide particles (A) may be achieved.

It is preferred that the group X containing a functional group having a pKa of 14 or less is directly bonded to a nitrogen atom in the repeating unit containing the nitrogen atom, but the nitrogen atom of the repeating unit containing the nitrogen atom and the group X may be linked through covalent bonding or through ionic bonding to form a salt.

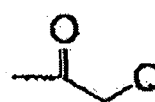
The group X containing a functional group having a pKa of 14 or less in the present invention particularly preferably has a structure represented by the general formula (V-1), the general formula (V-2), or the general formula (V-3).



Formula(V-1)



Formula(V-2)



Formula(V-3)

In the general formula (V-1) and the general formula (V-2),

U represents a single bond or a divalent linking group.

Each of d and e independently represents 0 or 1.

In the general formula (V-3), Q represents an acyl group or an alkoxycarbonyl group.

Examples of the divalent linking group represented by U include alkylene (more specifically, for example, -CH₂-, -CH₂CH₂-, -CH₂CHMe-, -(CH₂)₅-, -CH₂CH(n-C₁₀H₂₁)-, and the like), oxygen-containing alkylene (more specifically, for example, -CH₂OCH₂-, -CH₂CH₂OCH₂CH₂- and the like), an arylene group (for example, phenylene, tolylene, biphenylene, naphthylene, furanylene, pyrrolylene and the like), alkyleneoxy (for example, ethyleneoxy, propyleneoxy, phenyleneoxy and the like), and the like, but preferably an alkylene group having from 1 to 30 carbon atoms, or an arylene group having from 6 to 20 carbon atoms, and most preferably alkylene having from 1 to 20 carbon atoms, or an arylene group having from 6 to 15 carbon atoms. From the viewpoint of productivity, d is preferably 1, and e is preferably 0.

Q represents an acyl group or an alkoxycarbonyl group. As the acyl group in Q, an acyl group having from 1 to 30 carbon atoms (for example, formyl, acetyl, n-propanoyl, benzoyl and the like) is preferred, and acetyl is particularly preferred. As the alkoxycarbonyl group in Q, an alkoxycarbonyl group having from 2 to 30 carbon atoms (for example, a methoxycarbonyl group, an ethoxycarbonyl group, n-propoxycarbonyl group and the like) are

preferred. As Q, an acyl group is particularly preferred, and an acetyl group is preferred from the viewpoint of easy production and raw material availability (precursor X' of X).

The group X in the present invention is preferably bonded to a nitrogen atom of the repeating unit that contains the nitrogen atom. Accordingly, the dispersibility and dispersion stability of the metal oxide particles (A) are drastically improved. The reason is not clear, but it is thought as follows. That is, it is thought that the nitrogen atom of the repeating unit containing the nitrogen atom exists in the structure of an amino group, an ammonium group or an amide group, and the groups have interaction, such as hydrogen bonding and ionic bonding, with an acidic portion on the surface of the metal oxide particles (A), to be adsorbed. Moreover, X in the present invention functions as an acid group, and thus, can interact with a basic portion (when the metal oxide particles take on basic) or a metal atom (Ti of TiO₂ and the like) of the metal oxide particles (A). That is, it is thought that since the specific resin of the present invention may adsorb both the basic portion and the acidic portion of the metal oxide particles (A) with the nitrogen atom and the group X, the adsorption capacity is increased and thus, the dispersibility and storage stability are drastically improved.

It is thought that the X in the present invention imparts the solvent solubility to suppress resins from being precipitated over time, thereby contributing to dispersion stability.

The group X includes a functional group having a pKa of 14 or less as a partial structure thereto and thus functions as an alkaline soluble group. Accordingly, it is thought that when the resin is used in a curable composition or the like so as to impart an energy on a coating film and partially cure the coating film, and dissolve an unexposed part to remove the part and form a pattern, the developability into an alkaline developing solution in the uncured region is improved, and dispersibility, dispersion stability and developability may be established.

The content of the functional group having a pKa of 14 or less in X is not particularly limited, but it is preferably from 0.01 mmol to 5 mmol, and most preferably from 0.05 mmol to 1 mmol, based on 1 g of the specific resin of the present invention. Within this range, the dispersibility and dispersion stability of the metal oxide particles (A) are improved, and when the resin is used in a curable composition, the developability in the uncured part becomes excellent. From the viewpoint of an acid value, the functional group is preferably contained in an amount such that the acid value of the specific resin is from 5 mg KOH/g to 50 mg KOH/g from the viewpoint of developability when the specific resin of the present invention is used in the curable composition having a pattern forming property.

(Oligomer chain or polymer chain Y having number of atoms of from 40 to 10,000)

Examples of Y include known polymer chains such as polyester, polyamide, polyimide and poly(meth)acrylic acid ester, which may be linked to the main chain moiety of the specific resin. The linking portion of Y to the specific resin is preferably a terminal end of the oligomer chain or polymer chain Y.

Y is preferably bonded to a nitrogen atom of at least one repeating unit containing the nitrogen atom, selected from a poly(lower alkyleneimine)-based repeating unit, a polyallylamine repeating unit, a polydiallylamine-based repeating unit, a metaxylenediamine-epichlorohydrin polycondensate-based repeating unit and a polyvinylamine-based repeating unit. The bonding mode between Y and the main chain moiety such as at least one repeating unit containing a nitrogen atom, selected from a poly(lower alkyleneimine)-based repeating unit, a polyallylamine repeating unit, a polydiallylamine-based repeating unit, a metaxylenediamine-epichlorohydrin polycondensate-based repeating unit and a polyvinylamine-based repeating unit is covalent bonding, ionic bonding, or a combination of covalent bonding and ionic bonding. The ratio of the bonding modes of Y and the main chain moiety is in the range of covalent bonding: ionic bonding = from 100:0 to 0:100, preferably from 95:5 to 5:95 and most preferably from 90:10 to 10:90. When the ratio is out of the range, the dispersibility and dispersion stability are deteriorated and the solvent solubility is also decreased.

To a nitrogen atom of the repeating unit that contains the nitrogen atom, Y is preferably amide-bonded, or ionically bonded as carboxylate.

The number of atoms of the oligomer chain or polymer chain Y is preferably from 50 to 5,000 and more preferably from 60 to 3,000, from the viewpoint of dispersibility, dispersion stability and developability.

When the number of atoms per the oligomer chain or polymer chain Y is less than 40, the graft chain is short, and thus the sterically repulsive effect may be decreased, resulting in deteriorating the dispersibility. Meanwhile, when the number of atoms per the oligomer chain or polymer chain Y is more than 10,000, the oligomer chain or polymer chain Y is too long, and thus adsorptive force to the metal oxide particles may decrease, resulting in reducing dispersibility.

The number average molecular weight of Y may be measured by a polystyrene converted value by a GPC method. The number average molecular weight of Y is particularly preferably from 1,000 to 50,000 and most preferably from 1,000 to 30,000 from

the standpoint of dispersibility, dispersion stability and developability.

Preferably two or more, and most preferably five or more of the side chain structures represented by Y are bonded to the main chain linkage in one molecule of the resin.

In particular, Y preferably has a structure represented by the general formula (III-1).



Formula(III-1)

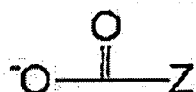
In the general formula (III-1), Z is a polymer or oligomer having a polyester chain as a partial structure, and represents a residue except the carboxyl group from a polyester having a free carboxylic acid represented by the following general formula (IV).



Formula(IV)

In the general formula (IV), Z is the same as Z in the general formula (III-1).

When the specific resin contains a repeating unit represented by the general formula (I-3) or the general formula (II-3), Y' is preferably represented by the general formula (III-2).



Formula(III-2)

In the general formula (III-2), Z is the same as Z in the general formula (III-1).

A polyester having a carboxyl group at one end (polyester represented by the general formula (IV)) may be obtained by polycondensation (IV-1) of carboxylic acid and lactone, polycondensation (IV-2) of a hydroxy group-containing carboxylic acid, polycondensation (IV-3) of a dihydric alcohol and a divalent carboxylic acid (or a cyclic acid anhydride), and the like.

The carboxylic acid used in the polycondensation reaction (IV-1) of carboxylic acid and lactone may be an aliphatic carboxylic acid (preferably a straight-chained or branched carboxylic acid having from 1 to 30 carbon atoms, for example, formic acid, acetic acid, propionic acid, butyric acid, valeric acid, n-hexanoic acid, n-octanoic acid, n-decanoic acid,

n-dodecanoic acid, palmitic acid, 2-ethylhexanoic acid, cyclohexanoic acid and the like), a hydroxy group-containing carboxylic acid (preferably a straight-chained or branched hydroxy group-containing carboxylic acid having from 1 to 30 carbon atoms, for example, glycolic acid, lactic acid, 3-hydroxypropionic acid, 4-hydroxydodecanoic acid, 5-hydroxydodecanoic acid, ricinoleic acid, 12-hydroxydodecanoic acid, 12-hydroxystearic acid, 2,2-bis(hydroxymethyl)butyric acid, and the like), but particularly preferably a straight-chained aliphatic carboxylic acid having from 6 to 20 carbon atoms or a hydroxy group-containing carboxylic acid having from 1 to 20 carbon atoms. These carboxylic acids may be used in a mixture. As the lactone, a known lactone may be used, and examples thereof include β -propiolactone, β -butyrolactone, γ -butyrolactone, γ -hexanolactone, γ -octanolactone, δ -valerolactone, δ -hexanolactone, δ -octanolactone, ϵ -caprolactone, δ -dodecanolactone, α -methyl- γ -butyrolactone and the like, and particularly preferably ϵ -caprolactone from the viewpoint of reactivity and availability.

These lactones may be used in combination of plural kinds thereof.

The feed molar ratio of the carboxylic acid and the lactone at the time of the reaction depends on the molecular weight of a target polyester chain, and thus the ratio may not be exclusively determined, but carboxylic acid:lactone = from 1:1 to 1:1,000 is preferred, and from 1:3 to 1:500 is most preferred.

The hydroxy group-containing carboxylic acid in the polycondensation (IV-2) of the hydroxy group-containing carboxylic acid is the same as the hydroxy group-containing carboxylic acid in (IV-1), and the preferred ranges thereof are also the same.

The dihydric alcohol of the polycondensation reaction (IV-3) of the dihydric alcohol and divalent carboxylic acid (or cyclic acid anhydride) may be a straight-chained or branched aliphatic diol (preferably a diol having from 2 to 30 carbon atoms, for example, ethylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, 1,2-propanediol, 1,3-propanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol and the like), and particularly preferably an aliphatic diol having from 2 to 20 carbon atoms.

Examples of the divalent carboxylic acid include a straight-chained or branched divalent aliphatic carboxylic acid (preferably a divalent aliphatic carboxylic acid having from 1 to 30 carbon atoms, for example, succinic acid, maleic acid, adipic acid, sebacic acid, dodecanoic diacid, glutaric acid, suberic acid, tartaric acid, oxalic acid, malonic acid, and the like), and particularly preferably a divalent carboxylic acid having from 3 to 20 carbon atoms. Acid anhydride (for example, anhydrous succinic acid, anhydrous glutaric acid and the like),

which are equivalent to these divalent carboxylic acids, may also be used.

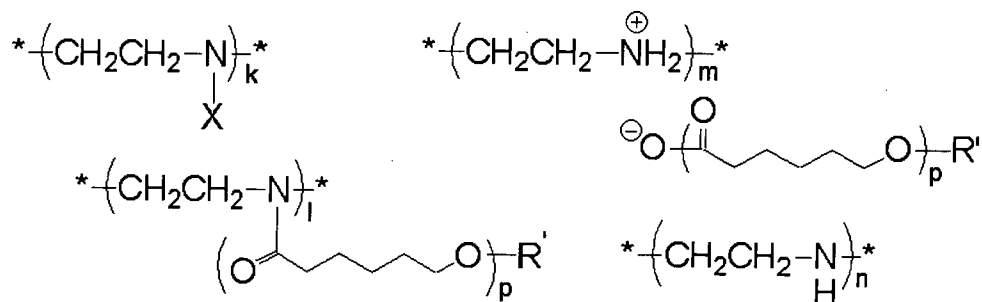
The divalent carboxylic acid and the dihydric alcohol are preferably fed at a molar ratio of 1:1. Accordingly, it is possible to introduce carboxylic acid into a terminal end.

The polycondensation at a time of preparation of polyester is preferably carried out with the addition of a catalyst. The catalyst is preferably a catalyst which functions as a Lewis acid, and examples thereof include a Ti compound (for example, $\text{Ti}(\text{OBu})_4$, $\text{Ti}(\text{O-Pr})_4$, and the like), an Sn compound (for example, tin octylate, dibutyltin oxide, dibutyltin laurate, monobutyltin hydroxybutyl oxide, stannic chloride, and the like), protonic acid (for example, sulfuric acid, paratoluenesulfonic acid, and the like), and the like. The amount of the catalyst is preferably from 0.01 mol% to 10 mol% and most preferably from 0.1 mol% to 5 mol%, based on the number of moles of the total monomers. The reaction temperature is preferably from 80°C to 250°C and most preferably from 100°C to 180°C. The reaction time varies depending on the reaction condition, but is usually from 1 hour to 24 hours.

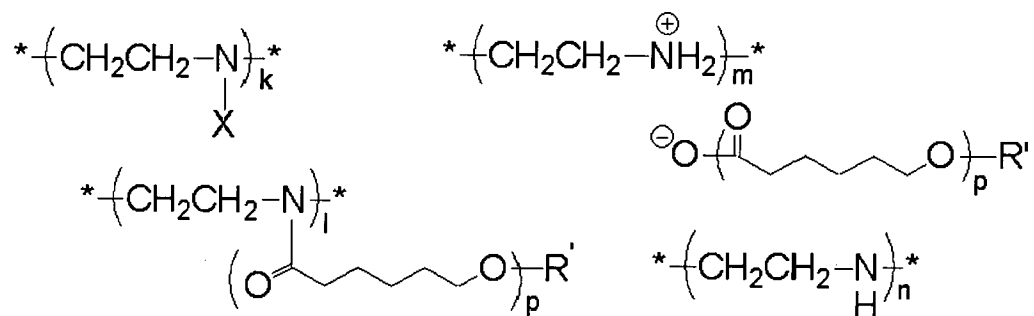
The number average molecular weight of the polyester may be measured by a polystyrene converted value by a GPC method. The number average molecular weight of the polyester is from 1,000 to 1,000,000, preferably from 2,000 to 100,000 and most preferably from 3,000 to 50,000. The molecular weight within this range may achieve both dispersibility and developability.

The polyester partial structure forming a polymer chain in Y is preferably a polyester, obtained by particularly the polycondensation (IV-1) of carboxylic acid and lactone, and the polycondensation (IV-2) of a hydroxy group-containing carboxylic acid, from the viewpoint of easy production.

The specific aspects [from (A-1) to (A-60)] of the specific resin of the present invention are shown below by the specific structures of the repeating units which the resin has and the combinations thereof, but the present invention is not limited thereto. In the following formulas, each of k, l, m and n represents a polymerization molar ratio of the repeating unit, k represents from 1 to 80, l represents from 10 to 90, m represents from 0 to 80, n represents from 0 to 70, and $k+l+m+n=100$. p and q represent a connectivity number of a polyester chain, and each of them independently represent from 5 to 100,000. R' represents a hydrogen atom or an alkylcarbonyl group.

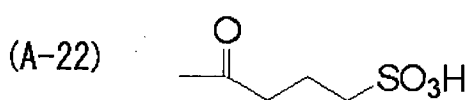
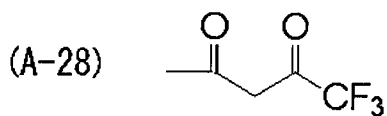
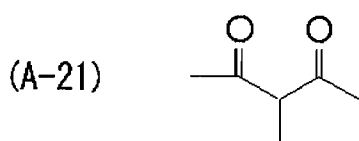
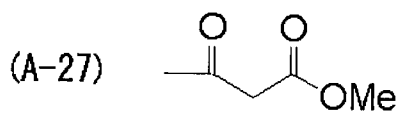
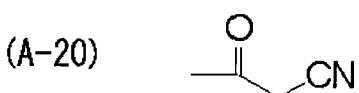
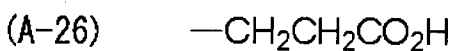
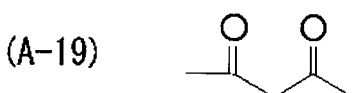
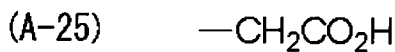
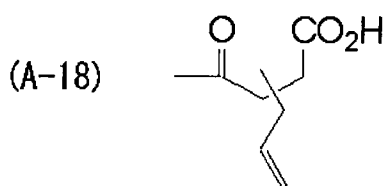
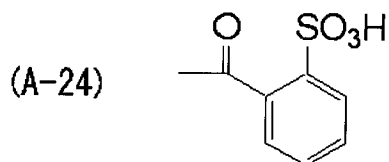
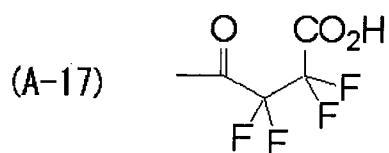
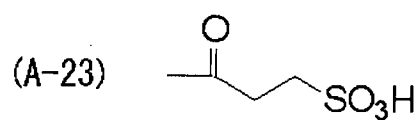
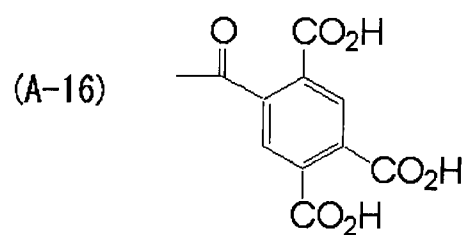


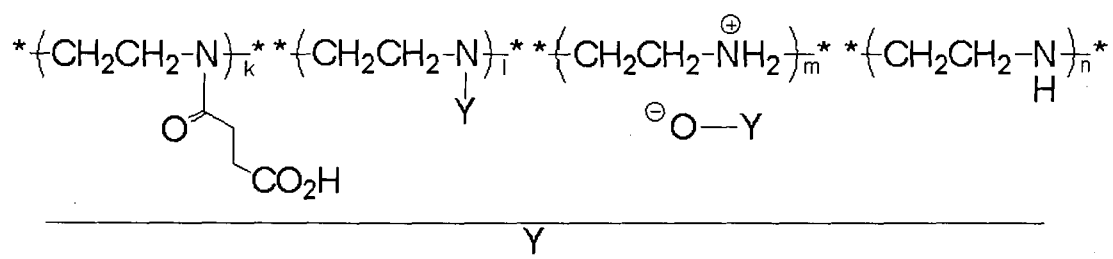
X		X	
(A-1)		(A-10)	
(A-2)		(A-11)	
(A-3)		(A-12)	
(A-4)		(A-13)	
(A-5)		(A-14)	
(A-6)		(A-15)	
(A-7)			
(A-8)			
(A-9)			



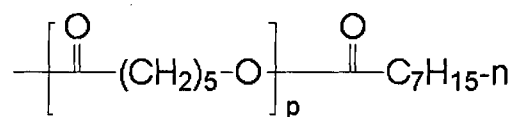
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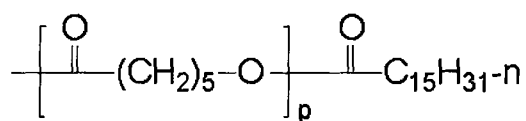




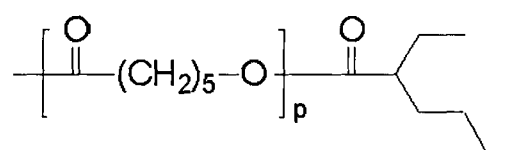
(A-29)



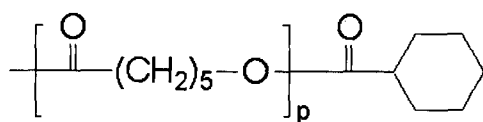
(A-30)



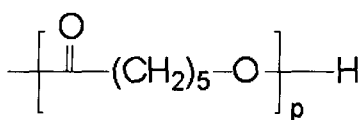
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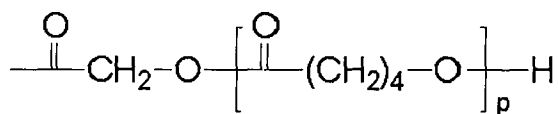
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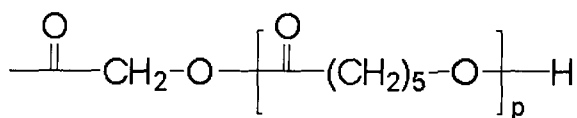
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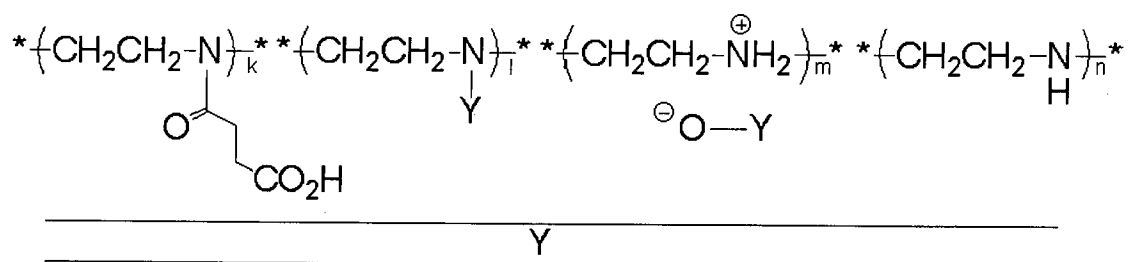


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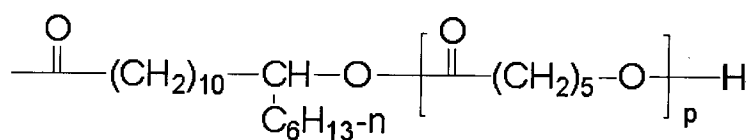


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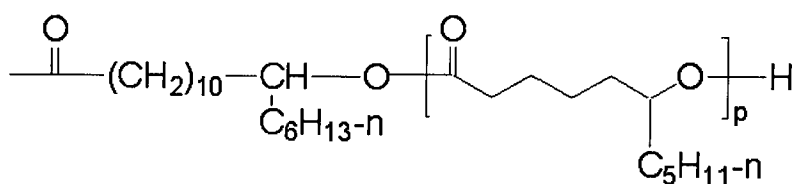




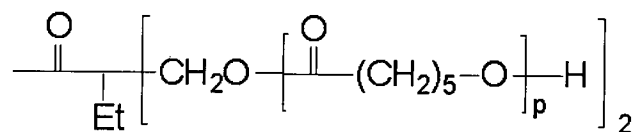
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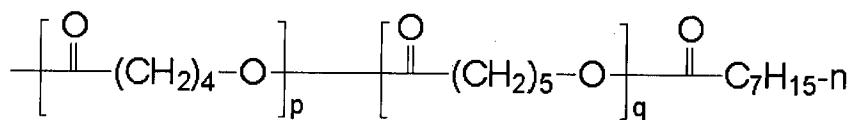
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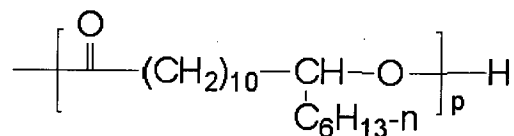
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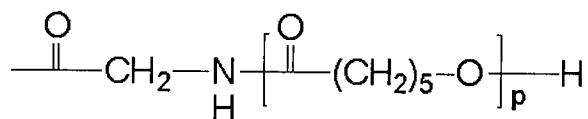
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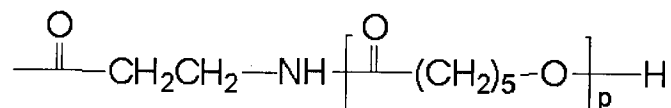
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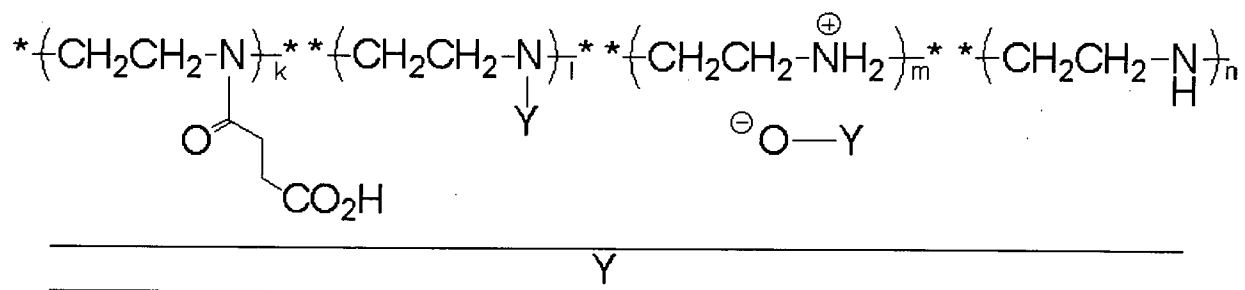


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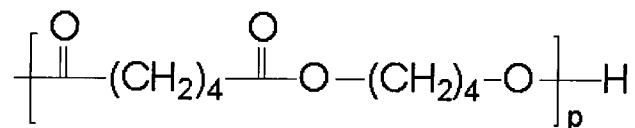


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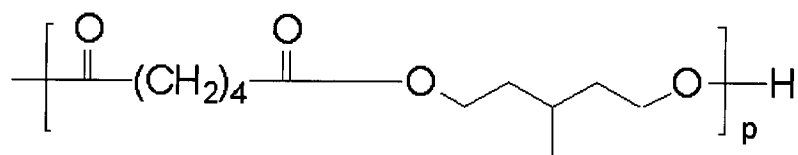




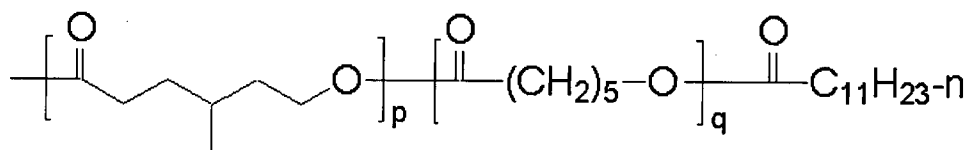
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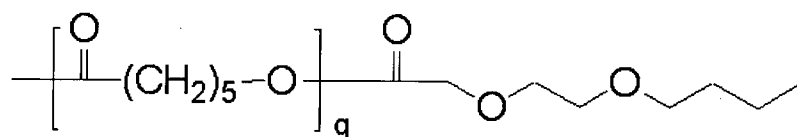
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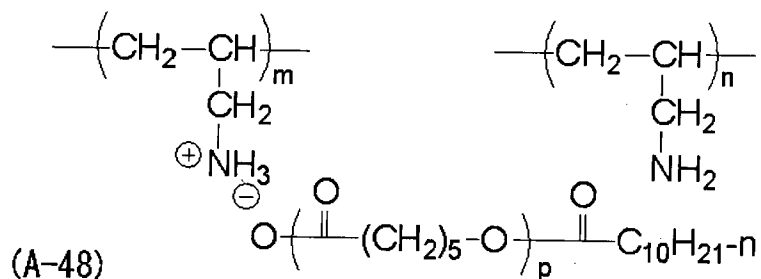
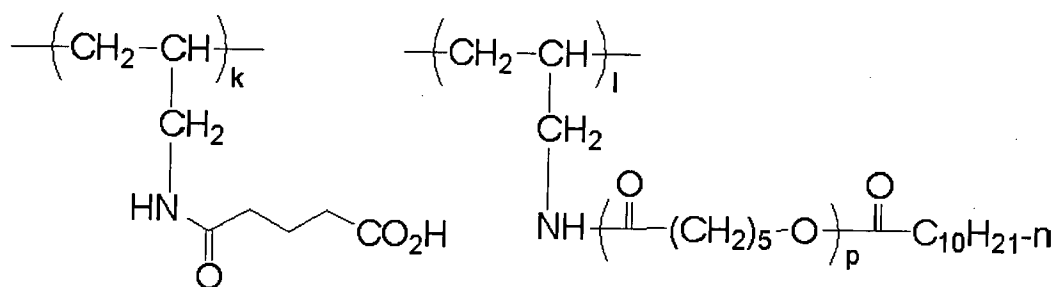
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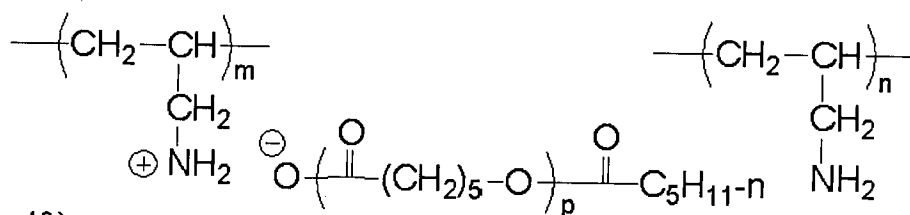
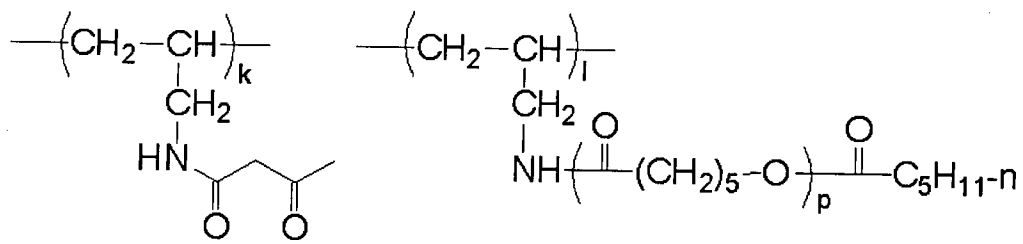
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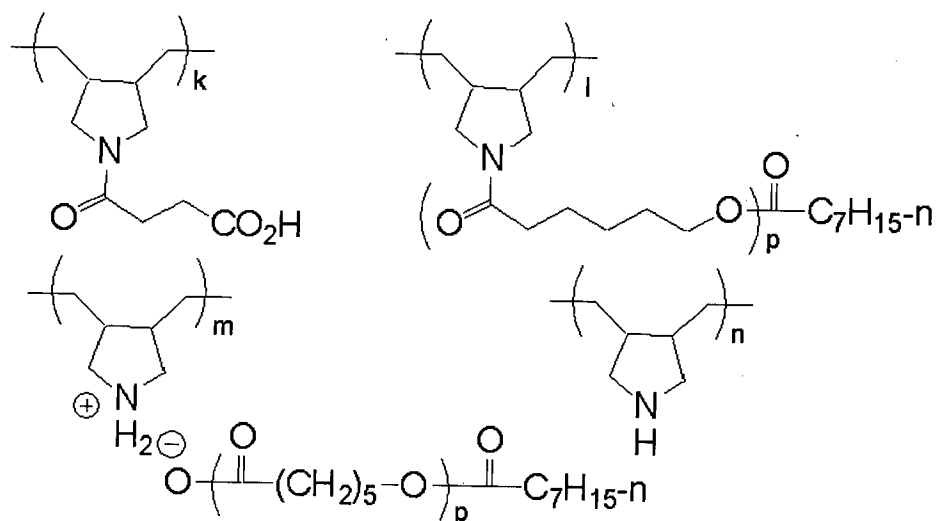
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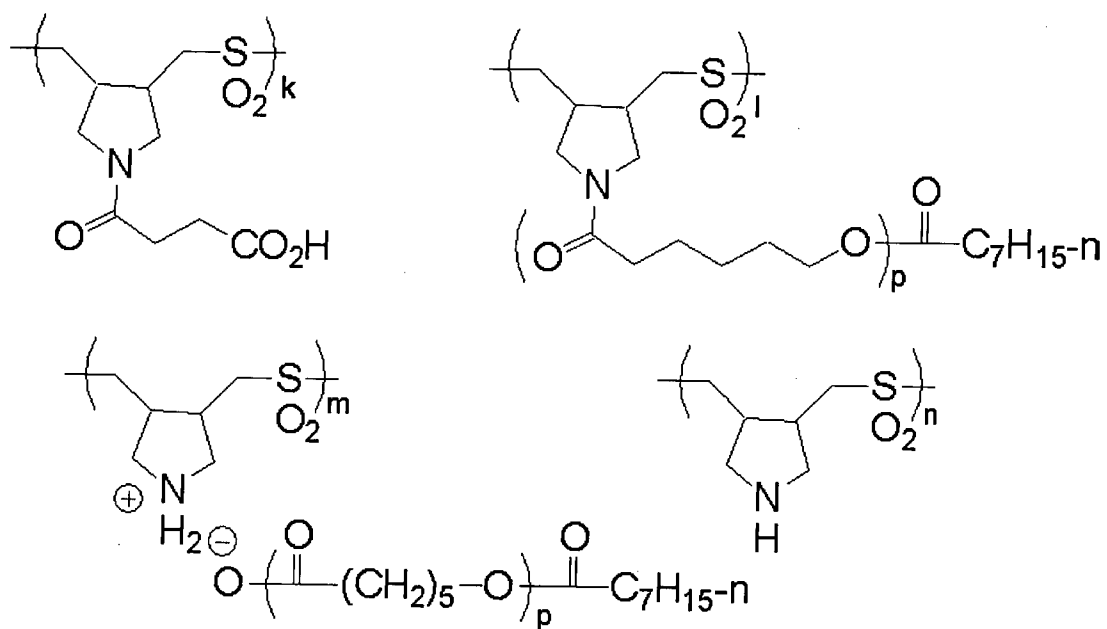
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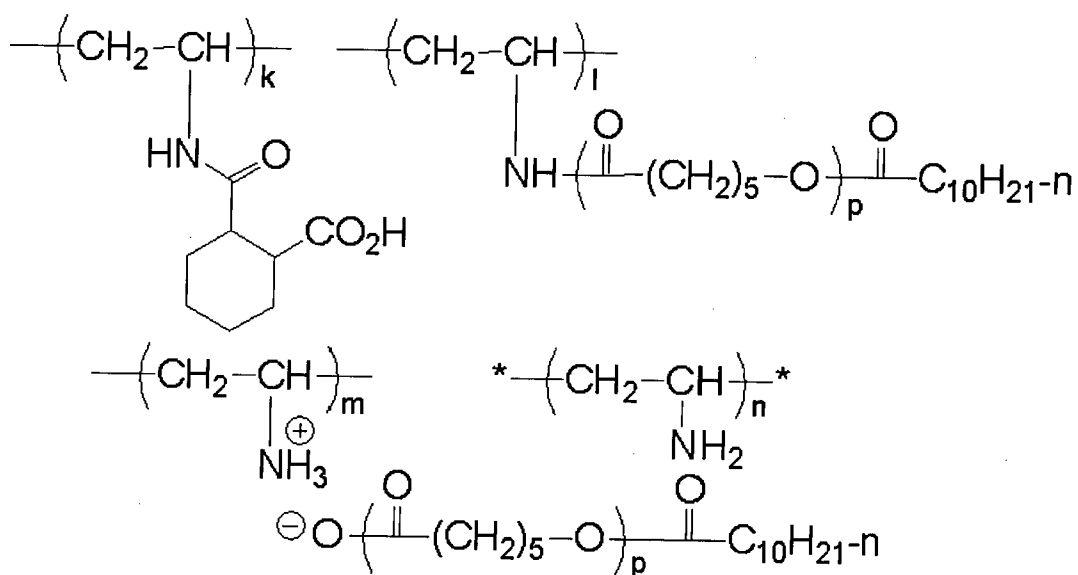
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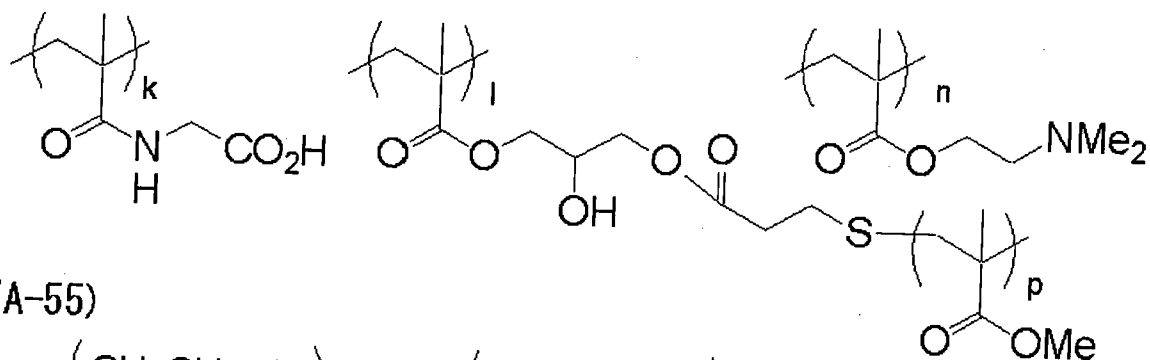
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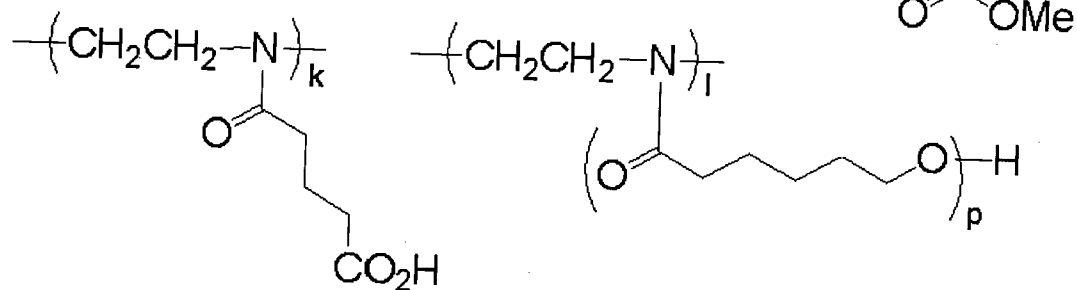
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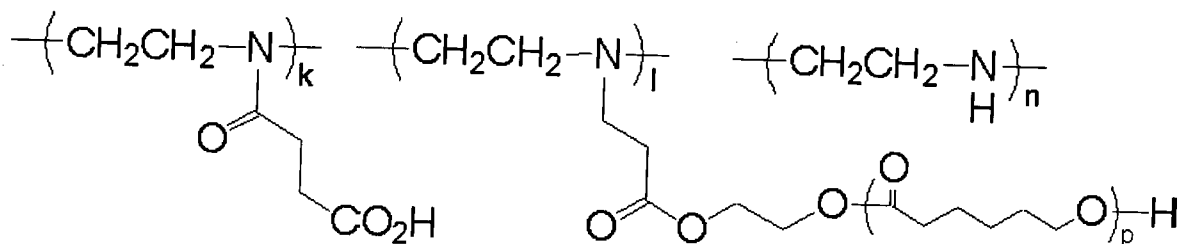
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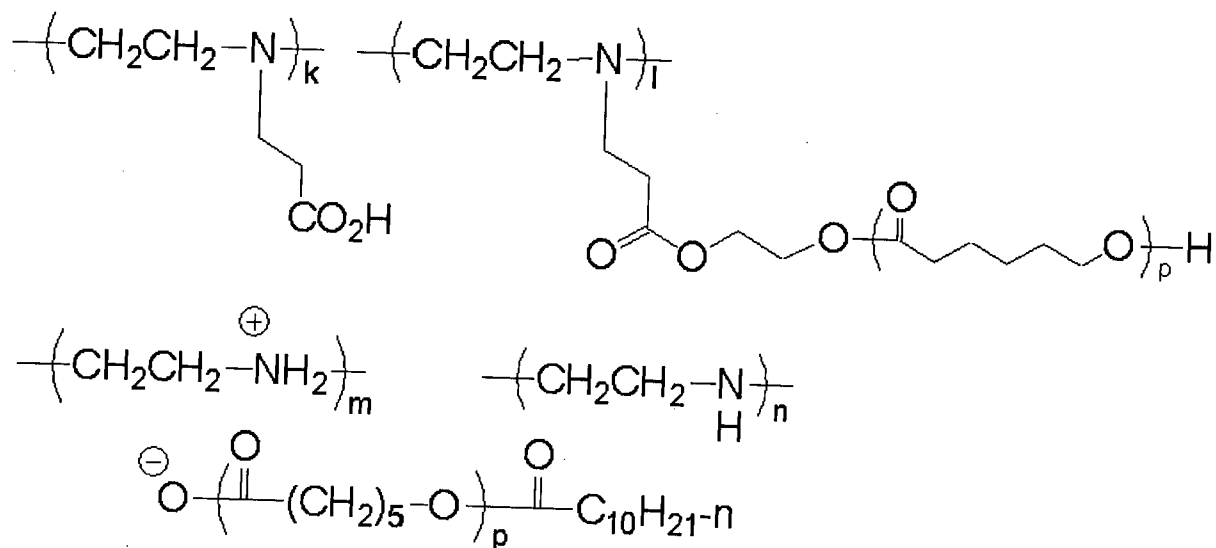
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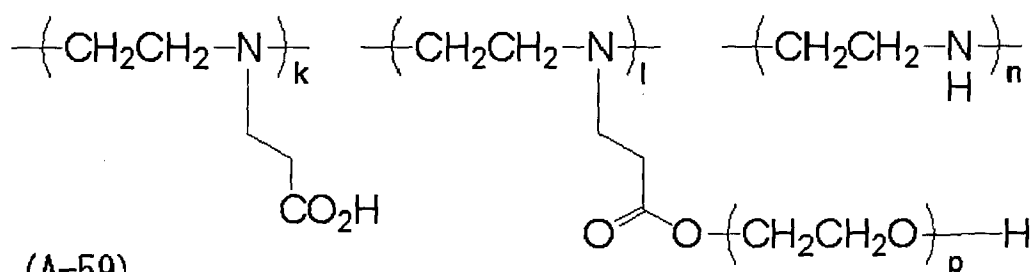
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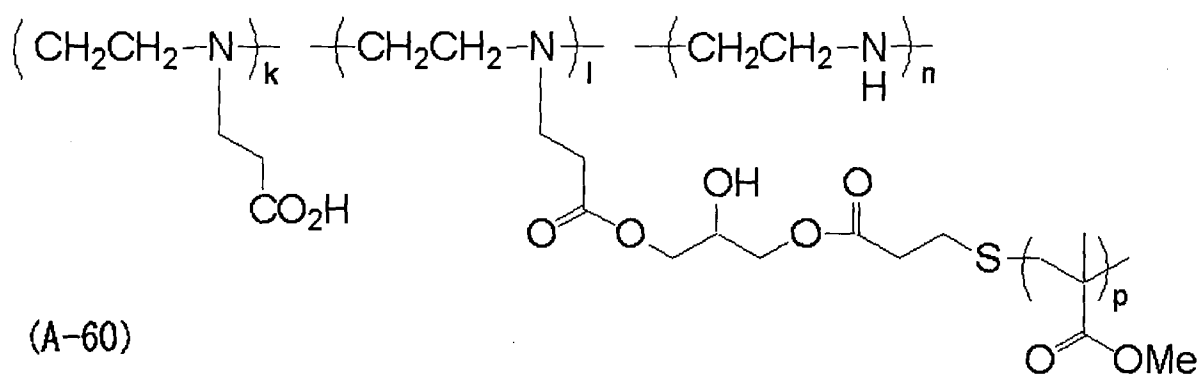
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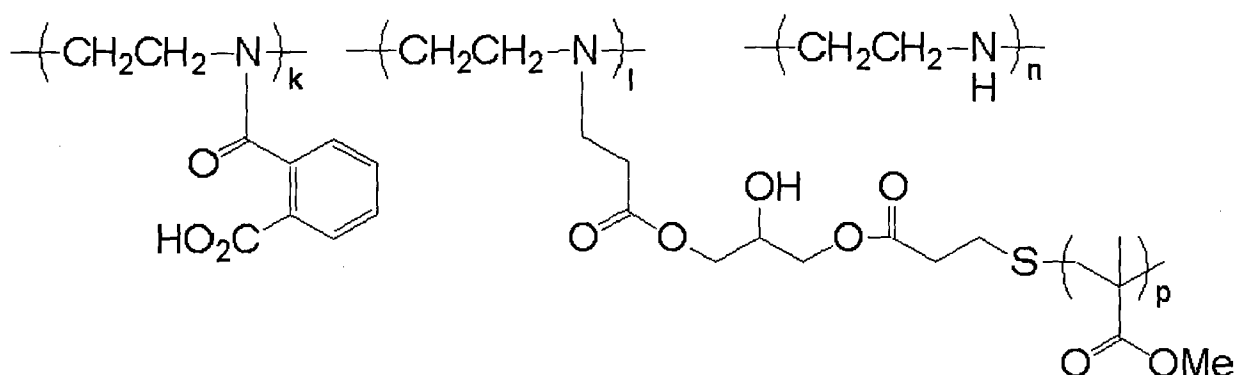
(A-58)



(A-59)



(A-60)



In order to synthesize the specific resin of the present invention, the specific resin may be prepared by (1) a method for reacting a resin having a primary or secondary amino group, a precursor x of X, and a precursor y of Y, (2) a method for polymerizing a monomer containing X and a macromonomer containing Y, or the like, and the specific resin is preferably prepared by first synthesizing a resin having a primary or secondary amino group in the main chain, and then allowing the resin to undergo a reaction with the precursor x of X and the precursor y of Y to introduce the reaction products to a nitrogen atom present in the main chain by a polymer reaction.

Examples of the resin having a primary or secondary amino group include an oligomer or polymer containing a primary or secondary amino group, which constitutes the main chain moiety containing a nitrogen atom, and for example, poly(lower alkyleneimine),

polyallylamine, polydiallylamine, a metaxylenediamine-epichlorohydrin polycondensate, polyvinylamine and the like. Among them, an oligomer or polymer consisting of poly(lower alkyleneimine) or polyallylamine is preferred.

The precursor x of the group X having a functional group having a pKa of 14 or less represents a compound which may react with the resin having a primary or secondary amino group to introduce X into the main chain.

Examples of the x include cyclic carboxylic acid anhydride (cyclic carboxylic acid anhydride having from 4 to 30 carbon atoms is preferred, and for example, succinic acid anhydride, glutaric acid anhydride, itaconic acid anhydride, maleic acid anhydride, allyl succinic acid anhydride, butyl succinic acid anhydride, n-octyl succinic acid anhydride, n-decyl succinic acid anhydride, n-dodecyl succinic acid anhydride, n-tetradecyl succinic acid anhydride, n-dococenyl succinic acid anhydride, (2-hexen-1-yl)succinic acid anhydride, (2-methylpropen-1-yl)succinic acid anhydride, (2-dodecen-1-yl)succinic acid anhydride, n-octenyl succinic acid anhydride, (2,7-octanediene-1-yl)succinic acid anhydride, acetyl malic acid anhydride, diacetyl tartaric acid anhydride, hex acid anhydride, cyclohexane-1,2-dicarboxylic acid anhydride, 3- or 4-methyl cyclohexane-1,2-dicarboxylic acid anhydride, tetrafluoro succinic acid anhydride, 3- or 4-cyclohexene-1,2-dicarboxylic acid anhydride, 4-methyl-4-cyclohexene-1,2-dicarboxylic acid anhydride, phthalic acid anhydride, tetrachlorophthalic acid anhydride, naphthalic acid anhydride, naphthalic acid anhydride, bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid dianhydride, pyromellitic acid dianhydride, meso-butane-1,2,3,4-tetracarboxylic acid dianhydride, 1,2,3,4-cyclopentane carboxylic acid dianhydride and the like), halogen atom-containing carboxylic acid (for example, chloroacetic acid, bromoacetic acid, iodoacetic acid, 4-chloro-n-butyric acid, and the like), sultone (for example, propanesultone, 1,4-butanedisultone, and the like), diketene, cyclic sulfocarboxylic acid anhydride (for example, 2-sulfobenzoic acid anhydride, and the like), a $-\text{COCH}_2\text{COCl}$ -containing compound (for example, ethylmalonyl chloride, and the like), or a cyano acetic acid chloride, and the like, and particularly preferably cyclic carboxylic acid anhydride, sultone and diketene from the viewpoint of productivity.

The precursor y of the oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000 represents a compound which may react with the resin having a primary or secondary amino group to introduce the oligomer chain or polymer chain Y.

The y is preferably an oligomer or polymer having the number of atoms of from 40 to 10,000, which has a group that may be covalently or ionically bonded to a nitrogen atom of the

specific resin at a terminal end, and particularly, an oligomer or polymer having the number of atoms of from 40 to 10,000, which has a free carboxyl group at one end is most preferred.

Examples of the y include a polyester represented by the general formula (IV), which has a free carboxylic acid at one end, a polyamide which has a free carboxylic acid at one end, a poly(meth)acrylic acid-based resin which has a free carboxylic acid at one end, and the like, but particularly a polyester represented by the general formula (IV), which contains a free carboxylic acid at one end, is most preferred.

The y may be synthesized by a known method, and for example, a method for preparing a polyester containing a free carboxylic acid at one end, which is represented by general formula (IV) by the polycondensation (IV-1) of carboxylic acid and lactone, the polycondensation (IV-2) of a hydroxy group-containing carboxylic acid or the polycondensation (IV-3) of a dihydric alcohol and a divalent carboxylic acid (or a cyclic acid anhydride) as described above can be exemplified. The polyamide containing a free carboxylic acid at one end may be prepared by self-condensation of an amino group-containing carboxylic acid (for example, glycine, alanine, β -alanine, 2-amino butyric acid and the like) and the like. The poly(meth)acrylic acid ester containing a free carboxylic acid at one end may be prepared by radical polymerization of (meth)acrylic acid-based monomers in the presence of a carboxyl group-containing chain transfer agent (for example, 3-mercaptopropionic acid and the like).

The specific resin of the present invention may be prepared by (a) a method in which a resin having a primary or secondary amino group is reacted with x and y simultaneously, (b) a method in which a resin having a primary or secondary amino group is first reacted with x, and then reacted with y, or (c) a method in which a resin having a primary or secondary amino group is first reacted with y, and then reacted with x. In particular, (c) a method in which a resin having a primary or secondary amino group is first reacted with y, and then reacted with x is preferred.

The reaction temperature may be suitably selected according to the conditions, but it is preferably from 20°C to 200°C and most preferably from 40°C to 150°C. The reaction time is preferably from 1 hour to 48 hours, and more preferably from 1 hour to 24 hours from the viewpoint of productivity.

The reaction may be carried out in the presence of a solvent. Examples of the solvent include water, a sulfoxide compound (for example, dimethylsulfoxide and the like), a ketone compound (for example, acetone, methyl ethyl ketone, cyclohexanone and the like), an ester

compound (for example, ethyl acetate, butyl acetate, ethyl propionate, propylene glycol 1-monomethyl ether 2-acetate and the like), an ether compound (for example, diethyl ether, dibutyl ether, tetrahydrofuran and the like), an aliphatic hydrocarbon compound (for example, pentane, hexane and the like), an aromatic hydrocarbon compound (for example, toluene, xylene, mesitylene, and the like), a nitrile compound (for example, acetonitrile, propionitrile and the like), an amide compound (for example, N,N-dimethyl formamide, N,N-dimethylacetamide, N-methylpyrrolidone and the like), a carboxylic acid compound (for example, acetic acid, propionic acid and the like), an alcohol compound (for example, methanol, ethanol, isopropanol, n-butanol, 3-methyl butanol, 1-methoxy-2-propanol and the like), and a halogen-based solvent (for example, chloroform, 1,2-dichloroethane and the like).

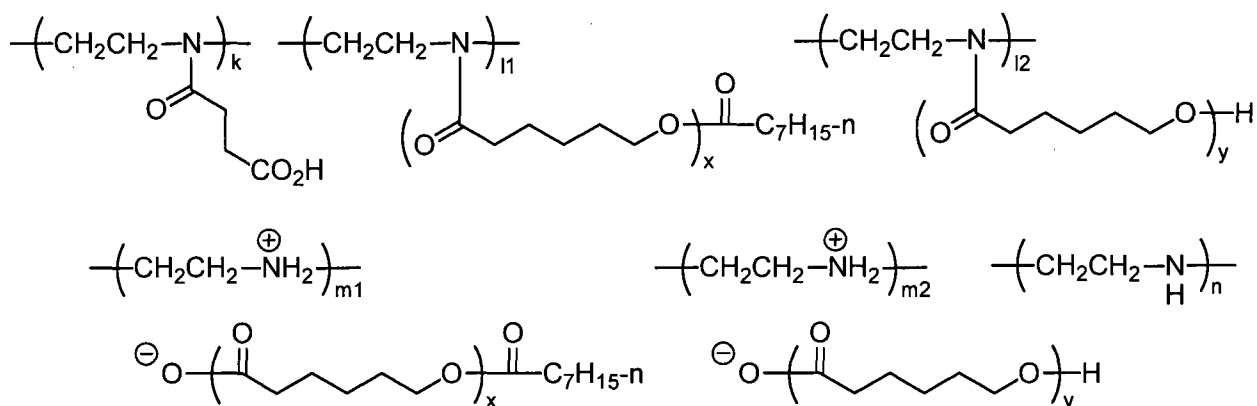
When a solvent is used, the solvent is preferably used at from 0.1 times by mass to 100 times by mass and most preferably from 0.5 times by mass to 10 times by mass, based on a substrate.

The specific resin of the present invention may be purified by a reprecipitation method. When the specific resin obtained by removing low molecular weight components by the reprecipitation method is used as a dispersing agent, the dispersion performance is improved.

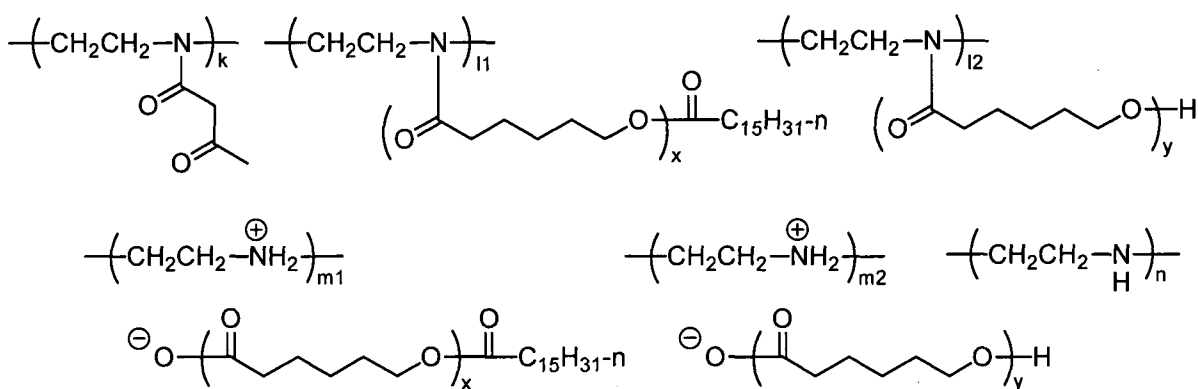
For the reprecipitation method, a hydrocarbon-based solvent such as hexane and an alcohol-based solvent such as methanol are preferably used.

The specific resin in the present invention thus obtained preferably has a weight average molecular weight of from 3,000 to 100,000 and more preferably from 5,000 to 55,000, as measured by a GPC method. The molecular weight in the above-described range is advantageous in that high developability and high storage stability can be achieved. The presence of a nitrogen atom in (i) the repeating unit containing the nitrogen atom in the specific resin of the present invention may be confirmed by a method such as an acid titration, and the presence of (ii) the functional group having a pKa of 14 or less and the bonding of the functional group to the nitrogen atom of the repeating unit may be confirmed by a method such as base titration, nuclear magnetic resonance spectroscopy and infrared spectroscopy. It may be confirmed by a method such as a nuclear magnetic resonance spectroscopy and a GPC method that (ii) the oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000 is contained in the side chain.

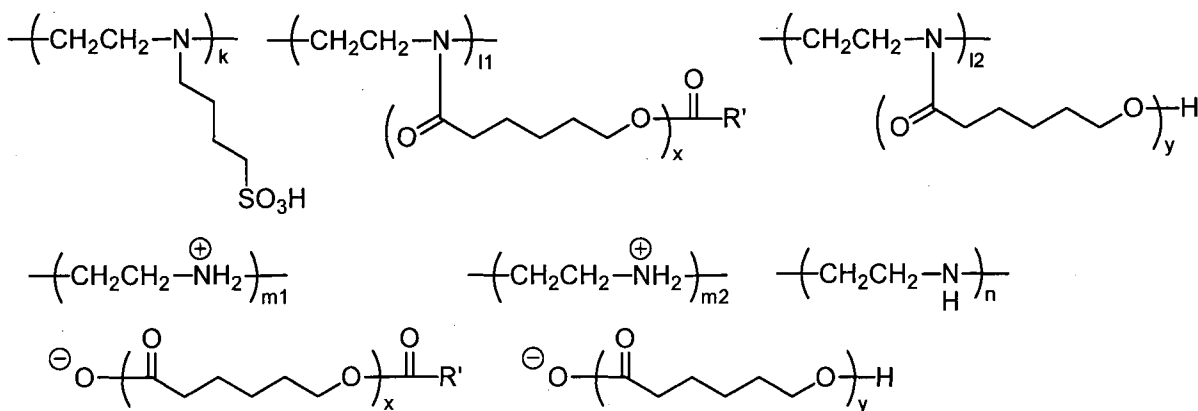
Hereinafter, specific examples of the specific resin of the present invention will be described along with the molecular weights thereof. R' represents an alkyl group.



$$k / (l1+l2) / (m1+m2) / n = 10/50/5/35 \quad x+y=40 \quad \text{Mw } 24,000 \quad \text{Mw/Mn} = 1.6$$

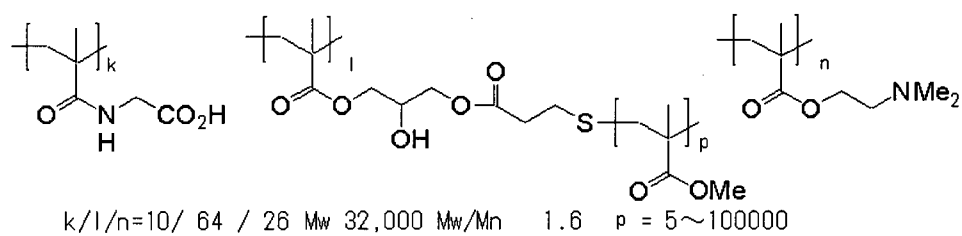
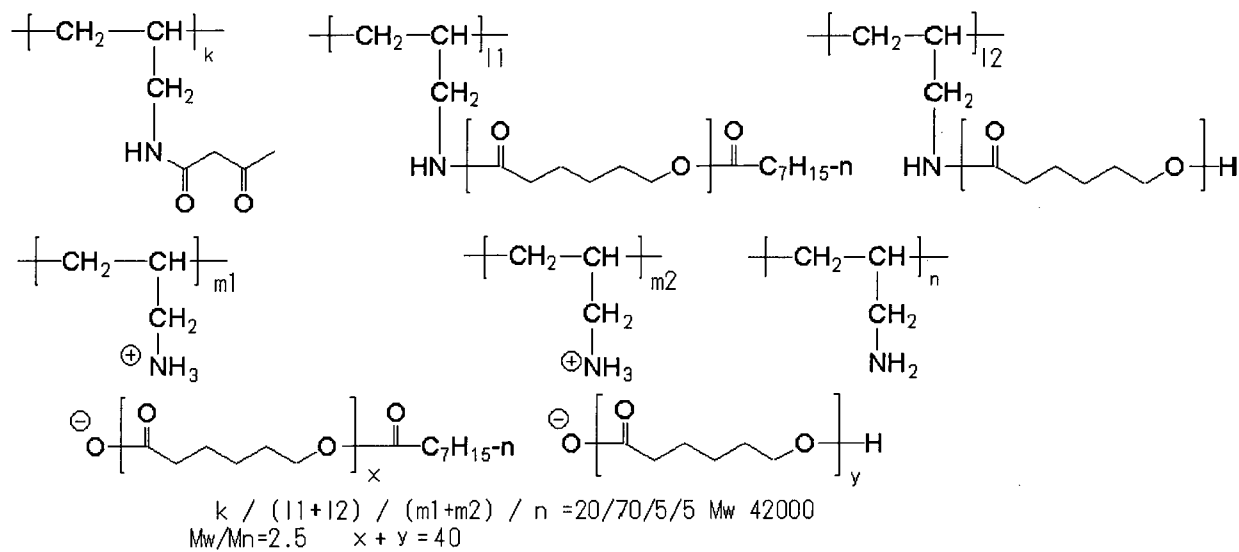


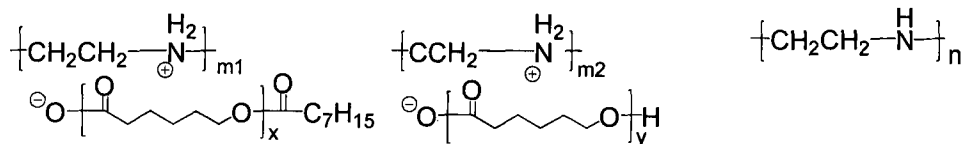
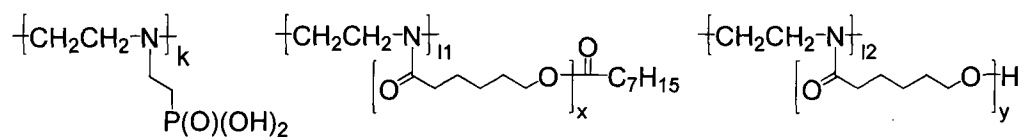
$$k / (l1+l2) / (m1+m2) / n = 20/40/5/35 \quad x+y=60 \quad \text{Mw } 18,000 \quad \text{Mw/Mn} = 1.6$$



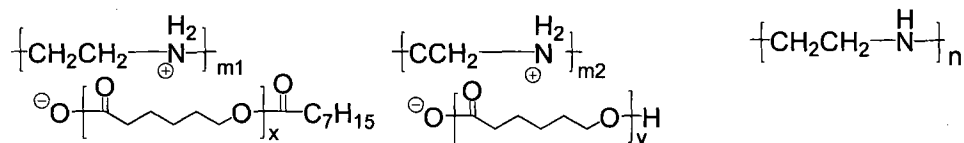
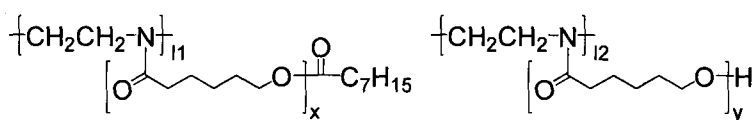
$$k / (l1+l2) / (m1+m2) / n = 5/60/10/25 \quad x+y=20 \quad \text{Mw } 12,000 \quad \text{Mw/Mn} = 1.6$$

$$\begin{array}{ccc}
 \left[\text{CH}_2 - \underset{\begin{array}{c} | \\ \text{CH}_2 \\ | \\ \text{HN} - \text{C}(=\text{O}) - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CO}_2\text{H} \end{array}}{\text{CH}} \right]_k &
 \left[\text{CH}_2 - \underset{\begin{array}{c} | \\ \text{CH}_2 \\ | \\ \text{HN} - \text{C}(=\text{O}) - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{O} - \text{C}(=\text{O}) - \text{C}_5\text{H}_{11-n} \end{array}}{\text{CH}} \right]_{11} &
 \left[\text{CH}_2 - \underset{\begin{array}{c} | \\ \text{CH}_2 \\ | \\ \text{HN} - \text{C}(=\text{O}) - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{O} - \text{C}(=\text{O}) - \text{C}_5\text{H}_{11-n} \end{array}}{\text{CH}} \right]_{12} \\
 \\
 \left[\text{CH}_2 - \underset{\begin{array}{c} | \\ \text{CH}_2 \\ | \\ \text{NH}_3^+ \end{array}}{\text{CH}} \right]_{m1} &
 \left[\text{CH}_2 - \underset{\begin{array}{c} | \\ \text{CH}_2 \\ | \\ \text{NH}_2^+ \end{array}}{\text{CH}} \right]_{m2} &
 \left[\text{CH}_2 - \underset{\begin{array}{c} | \\ \text{CH}_2 \\ | \\ \text{NH}_2 \end{array}}{\text{CH}} \right]_n \\
 \text{O}^- - \left[\text{C}(=\text{O}) - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{O} \right]_x - \text{C}_5\text{H}_{11-n} &
 \text{O}^- - \left[\text{C}(=\text{O}) - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{O} \right]_x - \text{C}_5\text{H}_{11-n} &
 \text{O}^- - \left[\text{C}(=\text{O}) - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{O} \right]_x - \text{H}
 \end{array}$$
$$\frac{k}{M_w/M_n=2.5} \cdot \frac{(I_1+I_2)}{x+y=20} \cdot \frac{(m_1+m_2)}{n} = \frac{30/60/5/5}{M_w} = 40,000$$

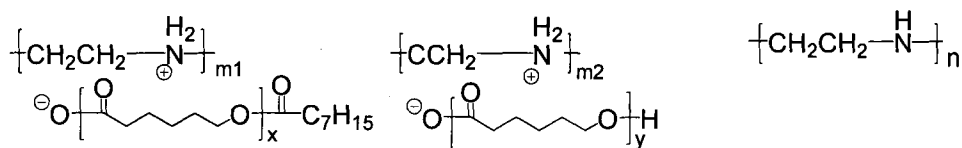
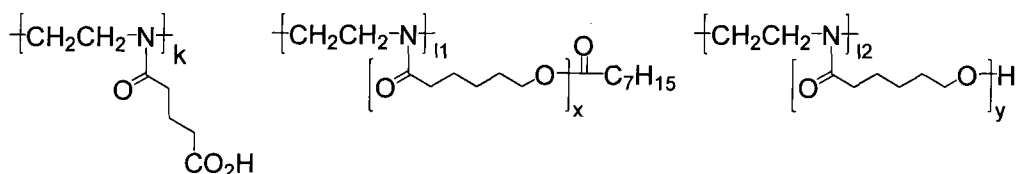




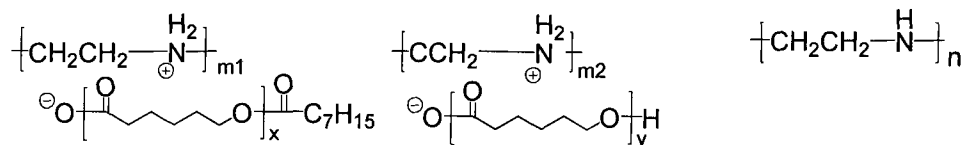
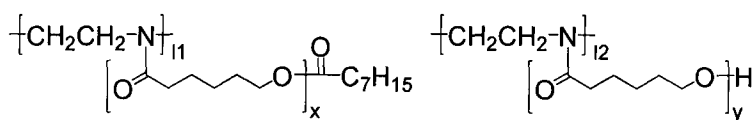
$$k / (l1+l2) / (m1+m2) / n = 5/40/20/35 \quad x+y=5 \quad \text{Mw } 15,000 \quad \text{Mw/Mn}=1.53$$



$$(l1+l2) / (m1+m2) / n = 55/35/10 \quad x+y=25 \quad \text{Mw } 6,000 \quad \text{Mw/Mn}=1.46$$



$$k / (l1+l2) / (m1+m2) / n = 5/40/35/20 \quad x+y=150 \quad \text{Mw } 38,000 \quad \text{Mw/Mn}=1.64$$



$$(l1+l2) / (m1+m2) / n = 50/20/30 \quad x+y=120 \quad \text{Mw } 28,000 \quad \text{Mw/Mn}=1.48$$

In the dispersion composition of the present invention, the specific resin may be used either alone or in combination of two or more thereof.

From the viewpoint of the dispersibility and the dispersion stability, the content of the specific resin is preferably in the range of from 10 mass% to 50 mass%, more preferably in the range of from 11 mass% to 40 mass% and even more preferably in the range of from 12 mass% to 30 mass%, based on the total solid content of the dispersion composition (or the curable composition as described below) of the present invention.

– Other Dispersion Resins –

The dispersion composition of the present invention may contain a dispersion resin (hereinafter, referred to as “other dispersion resins” in some cases) other than the specific resin, for the purpose of controlling the dispersibility of the metal oxide particles, and the like.

Examples of other dispersion resins that may be used in the present invention include a polymer dispersing agent [for example, polyamideamine and salts thereof, polycarboxylic acid and salts thereof, a high molecular weight unsaturated acid ester, modified polyurethane, modified polyester, modified poly(meth)acrylate, a (meth)acrylate copolymer and a naphthalenesulfonic acid-formalin condensate], polyoxyethylene alkyl phosphoric ester, polyoxyethylene alkylamine, alkanol amine, a pigment derivative, and the like.

The other dispersion resins may also be classified into a straight-chain polymer, a terminal end-modified polymer, a graft-type polymer and a block-type polymer, according to the structure thereof.

The other dispersion resins adhere to the surface of the metal oxide particles and function to prevent re-aggregation. Accordingly, examples of preferred structures of the resin include a terminal end-modified polymer, a graft-type polymer and a block-type polymer, each of which has an anchor moiety to the surface of the metal oxide particles.

Meanwhile, the other dispersion resins have an effect of modifying the surface of the metal oxide particles, thereby promoting adsorption of the dispersion resin.

Specific examples of other dispersion resins include “Disperbyk-101 (polyamideamine phosphate), 107 (carboxylic acid ester), 110 (a copolymer containing an acid group), 130 (polyamide), 161, 162, 163, 164, 165, 166 and 170 (a polymeric copolymer)”, “BYK-P104 and P105 (a high molecular weight unsaturated polycarboxylic acid)” which are manufactured by BYK Chemie GmbH, “EFKA 4047, 4050, 4010, 4165 (polyurethane-based), EFKA 4330, 4340 (block copolymer), 4400, 4402 (modified polyacrylate), 5010 (polyester amide), 5765 (a

high molecular weight polycarboxylic acid salt), 6220 (fatty acid polyester), 6745 (phthalocyanine derivative), 6750 (azo pigment derivative)” which are manufactured by EFKA; “AJISPER PB821, PB822” manufactured by Ajinomoto Fine-Techno Co., Inc., “FLOWLEN TG-710 (urethane oligomer)”, “Polyflow No. 50E, No. 300 (acrylic copolymer)” manufactured by KYOEISHA CHEMICAL Co., Ltd., “Disparlon KS-860, 873SN, 874, #2150 (aliphatic polyvalent carboxylic acid), #7004 (polyether ester), DA-703-50, DA-705, DA-725” manufactured by Kusumoto Chemicals Ltd., DEMOL RN, N (a naphthalenesulfonic acid-formalin polycondensate), “MS, C, SN-B (an aromatic sulfonic acid-formalin polycondensate)”, “HOMOGENOL L-18 (polymeric polycarboxylic acid)”, “EMULGEN 920, 930, 935, 985 (polyoxyethylene nonylphenyl ether)”, “ACETAMIN 86 (stearylamine acetate)” which are manufactured by Kao Corporation, “Solsperse 5000 (a phthalocyanine derivative), 22000 (an azo pigment derivative), 13240 (polyester amine), 3000, 17000, 27000 (a polymer having a functional moiety at a terminal thereof), 24000, 28000, 32000, 38500 (a graft-type polymer)” manufactured by The Lubrizol Corporation, “NIKKOL T106 (polyoxyethylene sorbitanmonooleate) and MYS-IEX (polyoxyethylene monostearate)” manufactured by Nikko Chemicals Co., Ltd., and the like.

These other dispersion resins may be used either alone or in combination of two or more thereof.

The dispersion composition (or the curable composition to be described below) of the present invention may or may not contain other dispersion resins, but when the composition contains other dispersion resins, the content of the other dispersion resins is preferably in the range of from 1 mass% to 20 mass% and more preferably in the range of from 1 mass% to 10 mass%, based on the total solid content of the dispersion composition (or the curable composition to be described below) of the present invention.

(C) Solvent

The dispersion composition of the present invention includes a solvent, and the solvent may be configured by using various organic solvents.

Examples of the organic solvents that may be used herein include acetone, methyl ethyl ketone, cyclohexane, ethyl acetate, ethylene dichloride, tetrahydrofuran, toluene, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol dimethyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, acetylacetone, cyclohexanone, diacetone alcohol, ethylene glycol monomethyl ether acetate, ethylene glycol

ethyl ether acetate, ethylene glycol monoisopropyl ether, ethylene glycol monobutyl ether acetate, 3-methoxypropanol, methoxymethoxyethanol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, 3-methoxypropyl acetate, N,N-dimethylformamide, dimethyl sulfoxide, γ -butyrolactone, methyl lactate, ethyl lactate and the like.

These solvents may be used either alone or in combination. The concentration of the solid content in the dispersion composition of the present invention is preferably from 2 to 60 mass%.

A method for preparing the dispersion composition of the present invention is not particularly limited, and a method for preparing a dispersion composition that is typically used may be applied. For example, preparation may be performed by mixing metal oxide particles (A), a resin (B) and a solvent (C), and subjecting the mixture to dispersion treatment using a circulation-type dispersion device (bead mill), and the like.

<Curable Composition>

A dispersible composition of the present invention is preferably a curable composition which is constituted such that the dispersion composition of the present invention includes a polymerizable compound (D) and a polymerization initiator, and if necessary, other components.

The dispersion composition may be made into a curable composition to form a film (representatively, a transparent film) having excellent dispersibility and dispersion stability, a very high refractive index, and a small difference in film thickness between the central portion and the peripheral portion even when the curable composition is applied on a large size wafer.

The present invention also relates to a transparent film formed by using the curable composition of the present invention.

A cured film to be obtained from the curable composition (a film that is formed by the curable composition and subsequently subjected to a curing reaction) has preferably a refractive index of from 1.72 to 2.60 and more preferably from 1.80 to 2.60.

The physical properties that the cured film has a refractive index of from 1.72 to 2.60 may be achieved by any means as long as the curable composition contains the dispersion composition of the present invention, a polymerizable compound (D) and a polymerization initiator (E), but the physical properties are suitably achieved, for example, by controlling the kind and content of the polymerizable composition (D) or a binder polymer which may be

further added, or containing the metal oxide particles (A) in the curable composition and simultaneously controlling the kind and content of the metal oxide particles.

In particular, the above-described physical properties may be preferably achieved by using the metal oxide particles as the above-described preferred example.

Moreover, the composition of the present invention is preferably a transparent composition, and more specifically, when a cured film having a film thickness of 1.0 μm is formed by the composition, the composition is a composition in which a light transmittance with respect to the thickness direction of the cured film is 90% or more over the entire wavelength region of from 400 nm to 700 nm.

That is, the transparent film of the present invention refers to a film in which a light transmittance with respect to the thickness direction of the film is 90% or more over the entire wavelength region of from 400 nm to 700 nm in a film thickness of 1.0 μm .

The physical properties of this light transmittance may be achieved by any means as long as the curable composition contains the dispersion composition of the present invention, a polymerizable compound (D) and a polymerization initiator (E), and are suitably achieved by controlling the kind and content of a polymerizable compound (D) or a binder polymer which may be further added. The physical properties of the light transmittance may be suitably achieved even by controlling the particle diameter of the metal oxide particles (A) or the kind and addition amount of the resin (B).

For the curable composition and the transparent film of the present invention, the fact that the light transmittance is 90% or more over the entire wavelength region of from 400 nm to 700 nm is an important factor in order to exhibit the characteristics which are required for, in particular, a microlens is an important factor.

The light transmittance is preferably 95% or more over the entire wavelength region of from 400 nm to 700 nm, more preferably 99% or more, and most preferably 100%.

Considering what has been described above, the curable composition of the present invention does not substantially contain a colorant (the content of the colorant is preferably 0 mass% based on the total solid content of the composition).

(D) Polymerizable Compound

The polymerizable compound (D) in the present invention is an addition-polymerizable compound that has at least one ethylenically unsaturated double bond, and is selected from the compounds having at least one and preferably two or more terminal end ethylenic unsaturated

bonds. Such compounds are widely known in the technical field, and these compounds may be used in the present invention without any particular limitation.

These compounds have chemical forms such as, for example, a monomer, a prepolymer, that is, a dimer, a trimer and an oligomer or mixtures thereof, and copolymers thereof. Examples of the monomers and copolymers thereof include an unsaturated carboxylic acid (for example, acrylic acid, methacrylic acid, itaconic acid, crotonic acid, isocrotonic acid, maleic acid and the like), and esters and amides thereof, and esters of an unsaturated carboxylic acid and an aliphatic polyhydric alcohol compound and amides of an unsaturated carboxylic acid and an aliphatic polyvalent amine compound are preferably used. An addition reaction product of unsaturated carboxylic acid esters or unsaturated carboxylic acid amides, which have a nucleophilic substituent group such as a hydroxyl group, an amino group and a mercapto group, with monofunctional or polyfunctional isocyanates or epoxies, a dehydration condensation reaction product of unsaturated carboxylic acid esters or unsaturated carboxylic acid amides with a monofunctional or polyfunctional carboxylic acid and the like, are suitably used. An addition reaction product of unsaturated carboxylic acid esters or unsaturated carboxylic acid amides, which have an electrophilic substituent group such as an isocyanate group and an epoxy group, with monofunctional or polyfunctional alcohols, amines or thiols; and a substitution reaction product of unsaturated carboxylic acid esters or unsaturated carboxylic acid amides, which have a releasable substituent group such as a halogen group and a tosyloxy group, with monofunctional or polyfunctional alcohols, amines or thiols, are also suitably used. As another example, the group of compounds obtained by replacing the unsaturated carboxylic acid with an unsaturated phosphonic acid, styrene, vinyl ether and the like may also be used.

Specific examples of the monomers of esters of an aliphatic polyhydric alcohol compound and an unsaturated carboxylic acid include acrylic acid esters, for example, ethylene glycol diacrylate, triethylene glycol diacrylate, 1,3-butanediol diacrylate, tetramethylene glycol diacrylate, propylene glycol diacrylate, neopentyl glycol diacrylate, trimethylolpropane triacrylate, trimethylolpropane tris(acryloyloxypropyl) ether, trimethylolethane triacrylate, hexanediol diacrylate, 1,4-cyclohexanediol diacrylate, tetraethylene glycol diacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol diacrylate, dipentaerythritol hexaacrylate, sorbitol triacrylate, sorbitol tetraacrylate, sorbitol pentaacrylate, sorbitol hexaacrylate, tris(acryloyloxyethyl) isocyanurate, a polyester acrylate oligomer, isocyanuric acid

EO-modified triacrylate and the like.

Examples of the methacrylic acid esters include tetramethylene glycol dimethacrylate, triethylene glycol dimethacrylate, neopentylglycol dimethacrylate, trimethylol propane trimethacrylate, triethylolethane trimethacrylate, ethylene glycol dimethacrylate, 1,3-butanediol dimethacrylate, hexanediol dimethacrylate, pentaerythritol dimethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, dipentaerythritol dimethacrylate, dipentaerythritol hexamethacrylate, sorbitol trimethacrylate, sorbitol tetramethacrylate, bis[p-(3-methacryloxy-2-hydroxypropoxy)phenyl]dimethyl methane, bis-[p-(methacryloxyethoxy)phenyl]dimethyl methane and the like.

Examples of the itaconic acid esters include ethylene glycol diitaconate, propylene glycol diitaconate, 1,3-butanediol diitaconate, 1,4-butanediol diitaconate, tetramethylene glycol diitaconate, pentaerythritol diitaconate, sorbitol tetraitaconate and the like.

Examples of the crotonic acid esters include ethylene glycol dicrotonate, tetramethylene glycol dicrotonate, pentaerythritol dicrotonate, sorbitol tetracrotonate, and the like. Examples of isocrotonic acid esters include ethylene glycol diisocrotonate, pentaerythritol diisocrotonate, sorbitol tetraisocrotonate and the like.

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

For example, aliphatic alcohol-based esters described in Japanese Patent Publication No. S51-47334 and Japanese Patent Application Laid-Open No. S57-196231, esters having an aromatic skeleton described in Japanese Patent Application Laid-Open Nos. S59-5240, S59-5241, and H2-226149, and esters containing an amino group described in Japanese Patent Application Laid-Open No. H1-165613, and the like, are also suitably used as examples of other esters. The above-described ester monomers may be used as a mixture.

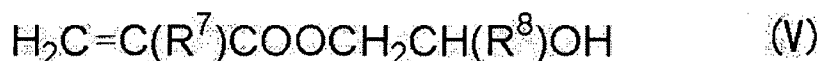
Specific examples of the monomers of amides of an aliphatic polyvalent amine compound and an unsaturated carboxylic acid include methylene bis-acrylamide, methylene bis-methacrylamide, 1,6-hexamethylene bis-acrylamide, 1,6-hexamethylene bis-methacrylamide, diethylenetriamine trisacrylamide, xylylene bisacrylamide, xylylene bismethacrylamide and the like.

Examples of other preferred amide-based monomers include a monomer having a cyclohexylene structure that is described in Japanese Patent Publication No. S54-21726.

Urethane-based addition polymerizable compounds prepared by using the addition reaction of isocyanate and a hydroxyl group are also suitable, and specific examples thereof

include vinyl urethane compounds containing two or more polymerizable vinyl groups in a molecule thereof, which are obtained by adding vinyl monomers containing a hydroxyl group, which are represented by the following Formula (V) to a polyisocyanate compound having two or more isocyanate groups in a molecule as described in Japanese Patent Publication No. S48-41708.

In Formula (V), each of R^7 and R^8 independently represents a hydrogen atom or a methyl group.



Urethane acrylates described in Japanese Patent Application Laid-Open No. S51-37193, Japanese Patent Publication Nos. H2-32293, and H2-16765, or urethane compounds having an ethylene oxide-based skeleton, described in Japanese Patent Publication Nos. S58-49860, S56-17654, S62-39417 and S62-39418 are also suitable. A curable composition having an excellent photosensitive speed may be obtained by using polymerizable compounds having an amino structure or a sulfide structure in a molecule, described in Japanese Patent Application Laid-Open Nos. S63-277653, S63-260909 and H1-105238.

Other examples thereof include polyfunctional acrylates or methacrylates such as polyester acrylates as described in Japanese Patent Application Laid-Open No. S48-64183, and Japanese Patent Publication Nos. S49-43191 and S52-30490, and epoxyacrylates obtained by reacting an epoxy resin with (meth)acrylic acid. Examples thereof also include specific unsaturated compounds described in Japanese Patent Publication Nos. S46-43946, H1-40337, and H1-40336, vinyl phosphonic acid compounds described in Japanese Patent Application Laid-Open No. H2-25493, and the like. In some cases, a structure containing a perfluoroalkyl group described in Japanese Patent Application Laid-Open No. S61-22048 is suitably used. Photocurable monomers or oligomers, described in the Journal of the Adhesion Society of Japan Vol. 20, No. 7, pp. 300 to 308 (1984) may be used.

For these polymerizable compounds, details of the method of use such as the structure of the compounds, single use or use of a combination and the amount to be added, may optionally be determined in accordance with the final performance design of the curable compounds. For example, the method is selected from the following viewpoint.

From the viewpoint of sensitivity, a structure having a high content of unsaturated groups per one molecule is preferred, and in many cases, bifunctionality or higher

functionality is preferred. In order to increase the strength of a cured film, trifunctionality or higher functionality is desirable. It is effective to use a method of controlling both the sensitivity and the strength by using compounds having different functionalities and/or different polymerizable groups (for example, acrylic acid ester, methacrylic acid ester, styrene-based compound and vinyl ether-based compound) in combination.

The selection and the method of use of the polymerizable compounds are also important factors for the compatibility with other components (for example, a polymerization initiator, metal oxide particles and the like) contained in the curable composition and for the dispersibility. For example, the compatibility may be increased by the use of a compound with low purity, or by the use of a combination of two or more kinds of other components. In some cases, a specific structure may be selected for the purpose of improving the adhesion to a hard surface such as a substrate.

-Compounds having two or more epoxy groups or oxetanyl groups in a molecule-

Examples of the compound having two or more epoxy groups in a molecule as a polymerizing compound (D) include epoxy resin of a bisphenol A type, epoxy resin of a bisphenol F type, epoxy resin of a phenol novolak type, epoxy resin of a cresol novolak type and an aliphatic epoxy resin.

They are available as the products on the market. Thus, examples of the epoxy resin of a bisphenol A type are JER827, JER828, JER834, JER1001, JER1002, JER1003, JER1055, JER1007, JER1009 and JER1010 (all manufactured by Japan Epoxy Resin) and EPICLON860, EPICLON1050, EPICLON1051 and EPICLON1055 (all manufactured by DIC Corporation); examples of the epoxy resin of a bisphenol F type are JER806, JER807, JER4004, JER4005, JER4007 and JER4010 (all manufactured by Japan Epoxy Resin), EPICLON830 and EPICLON835 (all manufactured by DIC Corporation) and LCE-21 and RE-602S (all manufactured by Nippon Kayaku Co., Ltd.); examples of the epoxy resin of a phenol novolak type are JER152, JER154, JER157S70 and JER157S65 (all manufactured by Japan Epoxy Resin) and EPICLON N-740, EPICLON N-770 and EPICLON N-775 (all manufactured by DIC Corporation); examples of the epoxy resin of a cresol novolak type are EPICLON N-660, EPICLON N-665, EPICLON N-670, EPICLON N-673, EPICLON N-680, EPICLON N-690 and EPICLON N-695 (all manufactured by DIC Corporation) and EOCN-1020 (manufactured by Nippon Kayaku Co., Ltd.); examples of the aliphatic epoxy resin are ADEKA RESIN EP-4080S, EP-4085S and EP-4088S (all manufactured by ADEKA), Celloxide 2021P, Celloxide 2081, Celloxide 2083, Celloxide 2085, EHPE3150, EPOLEAD PB 3600 and PB

4700 (all manufactured by Daicel Corporation) and Denacol EX-212L, EX-214L, EX-216L, EX-321L and EX-850L (all manufactured by Nagase Chemtex). Other than the above, ADEKA RESIN EP-4000S, EP-4003S, EP-4010S and EP-4011S (all manufactured by ADEKA), NC-2000, NC-3000, NC-7300, XD-1000, EPPN-501 and EPPN-502 (all manufactured by ADEKA) and JER1031S (manufactured by Japan Epoxy Resin) are exemplified.

Each of them may be used solely or two or more thereof may be used in combination.

Specific examples of the compound having two or more oxetanyl groups in a molecule include Aron Oxetan OXT-121, OXT-221, OX-SQ and PNOX (all manufactured by Toa Gosei Co., Ltd.).

It is preferred that the compound having oxetanyl group is used either solely or by mixing with a compound having epoxy group.

The content of (D) the polymerizable compound is preferably in the range of from 1 mass% to 50 mass%, more preferably in the range of from 3 mass% to 40 mass%, and even more preferably in the range of from 5 mass% to 30 mass%, based on the total solid content of the curable composition.

The content within the range is preferred, because the curability is excellent without deteriorating the refractive index.

(E) Polymerization Initiator

The polymerization initiator (E) which may be used in the present invention is a compound that initiates and promotes the polymerization of (D) the polymerizable compound and it is preferable that it is stable up to 45°C from the viewpoint of improving the curing in the heating process such as the processes (IV) and (b) in the method for forming a microlens as described below, but an ability to initiate polymerization during heating at a high temperature is excellent.

From the viewpoint of improving the curing in the exposure process by irradiation of radiation, such as processes (II), (b) and (d) in the method for forming a microlens as described below, it is preferred to have photosensitivity to light beam from ultraviolet region to visible region. The polymerization initiator may be an activator which causes any action with a photo-excited sensitizer to produce an active radical and may be an initiator which initiates the cationic polymerization according to the kind of the monomer.

It is preferred that the polymerization initiator contains at least one compound having a

molecular absorption coefficient of at least about 50 within the range of about from 300 nm to 800 nm (more preferably from 330 nm to 500 nm).

The polymerization initiator may be used either alone or in combination of two or more thereof.

Examples of (E) the polymerization initiator include an organic halide compound, an oxydiazole compound, a carbonyl compound, a ketal compound, a benzoin compound, an acridine compound, an organic peroxide compound, an azo compound, a coumarin compound, an azide compound, a metallocene compound, a hexaaryl biimidazole compound, an organic boric acid compound, a disulfonic acid compound, an oxime ester compound, an onium salt compound and an acyl phosphine(oxide) compound.

Specific examples of the organic halide compound include compounds described in "Bull. Chem. Soc. Japan", 42, 2924 (1969), Wakabayashi et al., U.S. Pat. No. 3,905,815, Japanese Patent Publication No. S46-4605, Japanese Patent Application Laid-Open Nos. S48-36281, S55-32070, S60-239736, S61-169835, S61-169837, S62-58241, S62-212401, S63-70243, and S63-298339, and "Journal of Heterocyclic Chemistry, 1 (No 3), (1970)", M. P. Hutt, and particularly, include an oxazole compound and an s-triazine compound, which are substituted with a trihalomethyl group.

As the s-triazine compound, an s-triazine derivative in which at least one mono-, di- or tri-halogen substituted methyl group is coupled with the s-triazine ring is more suitable, and specific examples of the s-triazine compound include 2,4,6-tris(monochloromethyl)-s-triazine, 2,4,6-tris(dichloromethyl)-s-triazine, 2,4,6-tris(trichloromethyl)-s-triazine, 2-methyl-4,6-bis(trichloromethyl)-s-triazine, 2-n-propyl-4,6-bis(trichloromethyl)-s-triazine, 2-(α,α,β -trichloroethyl)-4,6-bis(trichloromethyl)-s-triazine, 2-phenyl-4,6-bis(trichloromethyl)-s-triazine, 2-(p-methoxyphenyl)-4,6-bis(trichloromethyl)-s-triazine, 2-(3,4-epoxyphenyl)-4,6-bis(trichloromethyl)-s-triazine, 2-(p-chlorophenyl)-4,6-bis(trichloromethyl)-s-triazine, 2-[1-(p-methoxyphenyl)-2,4-butadienyl]-4,6-bis(trichloromethyl)-s-triazine, 2-styryl-4,6-bis(trichloromethyl)-s-triazine, 2-(p-methoxystyryl)-4,6-bis(trichloromethyl)-s-triazine, 2-(p-i-propyloxystyryl)-4,6-bis(trichloromethyl)-s-triazine, 2-(p-tolyl)-4,6-bis(trichloromethyl)-s-triazine, 2-(4-nathoxynaphthyl)-4,6-bis(trichloromethyl)-s-triazine,

2-phenylthio-4,6-bis(trichloromethyl)-s-triazine,
 2-benzylthio-4,6-bis(trichloromethyl)-s-triazine, 2,4,6-tris(dibromomethyl)-s-triazine,
 2,4,6-tris(tribromomethyl)-s-triazine, 2-methyl-4,6-bis(tribromomethyl)-s-triazine,
 2-methoxy-4,6-bis(tribromomethyl)-s-triazine and the like.

Examples of the oxydiazole compound include
 2-trichloromethyl-5-styryl-1,3,4-oxodiazole,
 2-trichloromethyl-5-(cyanostyryl)-1,3,4-oxodiazole,
 2-trichloromethyl-5-(naphtho-1-yl)-1,3,4-oxodiazole,
 2-trichloromethyl-5-(4-styryl)styryl-1,3,4-oxodiazole and the like.

[0130]

Examples of the carbonyl compound include benzophenone, benzophenone derivatives such as Michler's ketone, 2-methylbenzophenone, 3-methylbenzophenone, 4-methylbenzophenone, 2-chlorobenzophenone and 4-bromobenzophenone, 2-carboxybenzophenone, acetophenone derivatives such as 2,2-dimethoxy-2-phenyl acetophenone, 2,2-diethoxy acetophenone, 1-hydroxycyclohexyl phenyl ketone, α -hydroxy-2-methylphenyl propanone, 1-hydroxy-1-methylethyl-(p-isopropylphenyl)ketone, 1-hydroxy-1-(p-dodecylphenyl)ketone, 2-methyl-(4'-(methylthio)phenyl)-2-morpholino-1-propanone, 2-(dimethylamino)-2-[(4-methylphenyl)methyl]-1-[4-(4-morpholinyl)phenyl]-1-butanone, 1,1,1-trichloromethyl-(p-butylphenyl)ketone and 2-benzyl-2-dimethylamino-4-morpholinobutyrophenone, thioxanthone derivatives such as thioxanthone, 2-ethylthioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone, 2,4-dimethylthioxanthone and 2,4-diethylthioxanthone, 2,4-diisopropylthioxanthone, benzoate derivatives such as ethyl-p-dimethylaminobenzoate or ethyl-p-diethylaminobenzoate.

Examples of the ketal compound include benzyl methyl ketal, benzyl- β -methoxyethyl ethyl acetal and the like.

Examples of the benzoin compound include m-benzoin isopropyl ether, benzoin isobutyl ether, benzoin methyl ether, methyl-o-benzoyl benzoate and the like.

Examples of the acridine compound include 9-phenylacridine, 1,7-bis(9-acrydiny)heptane and the like.

Examples of the organic peroxide compound include trimethyl cyclohexanone peroxide, acetylacetone peroxide, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(tert-butylperoxy)cyclohexane, 2,2-bis(tert-butylperoxy)butane,

tert-butylhydroperoxide, cumene hydroperoxide, diisopropyl benzene hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide, 1,1,3,3-tetra-methylbutyl hydroperoxide, tert-butylcumyl peroxide, dicumyl peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 2,5-oxanoyl peroxide, succinic acid peroxide, benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, diisopropyl peroxydicarbonate, di-2-ethylhexyl peroxydicarbonate, di-2-ethoxyethyl peroxydicarbonate, dimethoxyisopropyl peroxycarbonate, di(3-methyl-3-methoxybutyl)peroxydicarbonate, tert-butyl peroxyacetate, tert-butyl peroxyipivalate, tert-butyl peroxyneodecanoate, tert-butyl peroxyoctanoate, tert-butylperoxylaurate, 3,3',4,4'-tetra-(t-butylperoxycarbonyl)benzophenone, 3,3',4,4'-tetra-(t-hexylperoxycarbonyl)benzophenone, 3,3',4,4'-tetra-(p-isopropylcumylperoxycarbonyl)benzophenone, carbonyl-di(t-butylperoxydihydrogen diphthalate), carbonyl-di(t-hexylperoxy dihydrogen diphthalate) and the like.

Examples of the azo compound include the azo compounds described in Japanese Patent Application Laid-Open No. H8-108621.

Examples of the coumarin compound include 3-methyl-5-amino-((s-triazin-2-yl)amino)-3-phenyl coumarin, 3-chloro-5-diethylamino-((s-triazin-2-yl)amino)-3-phenyl coumarin, 3-butyl-5-dimethylamino-((s-triazin-2-yl)amino)-3-phenyl coumarin and the like.

Examples of the azide compound include organic azide compounds described in U.S. Pat. Nos. 2,848,328, 2,852,379, and 2,940,853, 2,6-bis(4-azidobenzylidene)-4-ethylcyclohexanone (BAC-E) and the like.

Examples of the metallocene compound include various titanocene compounds described in Japanese Patent Application Laid-Open Nos. S59-152396, S61-151197, S63-41484, H2-249, H2-4705, and H5-83588, and specific examples thereof include dicyclopentadienyl-Ti-bis-phenyl, dicyclopentadienyl-Ti-bis-2,6-difluorophenyl-1-yl, dicyclopentadienyl-Ti-bis-2,4-difluorophenyl-1-yl, dicyclopentadienyl-Ti-bis-2,4,6-trifluorophenyl-1-yl, dicyclopentadienyl-Ti-bis-2,3,5,6-tetrafluorophenyl-1-yl, dicyclopentadienyl-Ti-bis-2,3,4,5,6-pentafluorophenyl-1-yl, di-methylcyclopentadienyl-Ti-bis-2,6-difluorophenyl-1-yl, dimethylcyclopentadienyl-Ti-bis-2,4,6-trifluorophenyl-1-yl, dimethylcyclopentadienyl-Ti-bis-2,3,5,6-tetrafluorophenyl-1-yl,

dimethylcyclopentadienyl-Ti-bis-2,3,4,5,6-pentafluorophenyl-1-yl, iron-arene complexes described in Japanese Patent Application Laid-Open Nos. H1-304453 and H1-152109, and the like.

As the biimidazole compound, for example, a hexaaryl biimidazole compound (lophine dimer compound) and the like are preferred.

Examples of the hexaaryl biimidazole compound include lophine dimers described in Japanese Patent Publication Nos. S45-37377 and S44-86516, and various compounds described in Japanese Patent Publication No. H6-29285, U.S. Pat. Nos. 3,479,185, 4,311,783, and 4,622,286 and the like, and specific examples thereof include 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetraphenylbiimidazole, 2,2'-bis(o-bromophenyl)-4,4',5,5'-tetraphenylbiimidazole, 2,2'-bis(o,p-dichlorophenyl)-4,4',5,5'-tetraphenylbiimidazole, 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetra(m-methoxyphenyl)biimidazole, 2,2'-bis(o,o'-dichlorophenyl)-4,4',5,5'-tetraphenylbiimidazole, 2,2'-bis(o-nitrophenyl)-4,4',5,5'-tetraphenylbiimidazole, 2,2'-bis(o-methylphenyl)-4,4',5,5'-tetraphenylbiimidazole, 2,2'-bis(o-trifluorophenyl)-4,4',5,5'-tetraphenylbiimidazole and the like.

Examples of the organic borate compound include organic borates described in Japanese Patent Application Laid-Open Nos. S62-143044, S62-150242, H9-188685, H9-188686, H9-188710, 2000-131837, and 2002-107916, Japanese Patent No. 2764769, and Japanese Patent Application Laid-Open No. 2001-16539, and "Rad Tech '98. Proceeding, in Chicago Apr. 19-22, 1998", Kunz, Martin, organic boron sulfonium complexes or organic boron oxosulfonium complexes described in Japanese Patent Application Laid-Open Nos. H6-157623, H6-175564, and H6-175561, organic boron iodonium complexes described in Japanese Patent Application Laid-Open Nos. H6-175554, and H6-175553, organic boron phosphonium complexes described in Japanese Patent Application Laid-Open No. H9-188710, organic boron transition-metal coordination complexes described in Japanese Patent Application Laid-Open Nos. H6-348011, H7-128785, H7-140589, H7-306527, H7-292014, and the like.

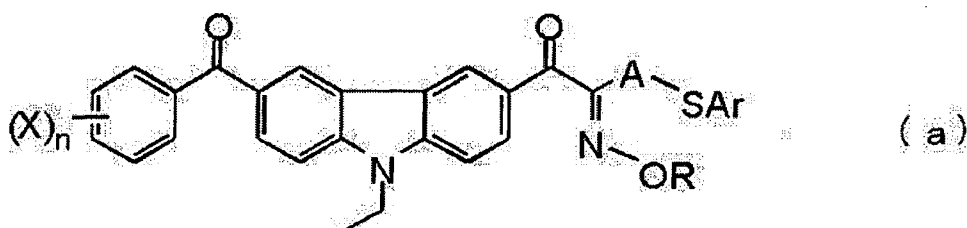
Examples of the disulfone compound include the compound described in Japanese Patent Application Laid-Open Nos. S61-166544 and 2002-328465, and the like.

From the viewpoint of the curability, the stability over time and difficulty in the coloration at the time of post-heating, oxime compounds are preferred as (E) the

polymerization initiator used in the present invention.

Examples of the oxime compounds include compounds described in J. C. S. Perkin II (1979) 1653-1660, J. C. S. Perkin II (1979) 156-162, Journal of Photopolymer Science and Technology (1995) 202-232, and Japanese Patent Application Laid-Open No. 2000-66385, compounds described in Japanese Patent Application Laid-Open No. 2000-80068, and Japanese Patent Application National Publication No. 2004-534797, and the like.

From the viewpoint of the sensitivity and the stability over time, the compound represented by the following general formula (a) is more preferred as the oxime compound to be used in the present invention.



In formula (a), each of R and X independently represents a monovalent substituent group, A represents a divalent organic group, and Ar represents an aryl group. n is an integer of from 0 to 5. When plural X's are present, each X may be the same as or different from every other X.

Examples of the monovalent substituent group represented by R in formula (a) preferably include monovalent non-metal atomic groups as shown below.

Examples of the monovalent non-metal atomic groups represented by R in formula (a) include an alkyl group which may have a substituent group, an aryl group which may have a substituent group, an alkenyl group which may have a substituent group, an alkynyl group which may have a substituent group, an alkylsulfinyl group which may have a substituent group, an arylsulfinyl group which may have a substituent group, an alkylsulfonyl group which may have a substituent group, an arylsulfonyl group which may have a substituent group, an acyl group which may have a substituent group, an alkoxycarbonyl group which may have a substituent group, an aryloxycarbonyl group which may have a substituent group, a phosphinoyl group which may have a substituent group, a heterocyclic group which may have a substituent group, an alkylthiocarbonyl group which may have a substituent group, an arylthiocarbonyl group which may have a substituent group, a dialkylamino carbonyl group which may have a substituent group, a dialkylamino thiocarbonyl group which may have a substituent group, and the like.

As the alkyl group which may have a substituent group, an alkyl group having from 1 to 30 carbon atoms is preferred, and examples thereof include a methyl group, an ethyl group, a propyl group, a butyl group, a hexyl group, an octyl group, a decyl group, a dodecyl group, an octadecyl group, an isopropyl group, an isobutyl group, a sec-butyl group, a t-butyl group, a 1-ethylpentyl group, a cyclopentyl group, a cyclohexyl group, a trifluoromethyl group, a 2-ethylhexyl group, a phenacyl group, a 1-naphthoylmethyl group, a 2-naphthoylmethyl group, a 4-methylsulfanylphenacyl group, a 4-phenylsulfanylphenacyl group, a 4-dimethylaminophenacyl group, a 4-cyanophenacyl group, a 4-methylphenacyl group, a 2-methylphenacyl group, a 3-fluorophenacyl group, a 3-trifluoromethylphenacyl group, a 3-nitrophenacyl group and the like.

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

As the alkenyl group which may have a substituent group, an alkenyl group having from 2 to 10 carbon atoms is preferred, and examples thereof include a vinyl group, an allyl group, a styryl group and the like.

As the alkynyl group which may have a substituent group, an alkynyl group having from 2 to 10 carbon atoms is preferred, and examples thereof include an ethynyl group, a propynyl group, a propargyl group and the like.

As the alkylsulfinyl group which may have a substituent group, an alkylsulfinyl group having from 1 to 20 carbon atoms is preferred, and examples thereof include a methylsulfinyl

group, an ethylsulfinyl group, a propylsulfinyl group, an isopropylsulfinyl group, a butylsulfinyl group, a hexylsulfinyl group, a cyclohexylsulfinyl group, an octylsulfinyl group, a 2-ethylhexylsulfinyl group, a decanoylsulfinyl group, a dodecanoylsulfinyl group, an octadecanoylsulfinyl group, a cyanomethylsulfinyl group, a methoxymethylsulfinyl group and the like.

As the arylsulfinyl group which may have a substituent group, an arylsulfinyl group having from 6 to 30 carbon atoms is preferred, and examples thereof include a phenylsulfinyl group, a 1-naphthylsulfinyl group, a 2-naphthylsulfinyl group, a 2-chlorophenylsulfinyl group, a 2-methylphenylsulfinyl group, a 2-methoxyphenylsulfinyl group, a 2-butoxyphenylsulfinyl group, a 3-chlorophenylsulfinyl group, a 3-trifluoromethylphenylsulfinyl group, a 3-cyanophenylsulfinyl group, a 3-nitrophenylsulfinyl group, a 4-fluorophenylsulfinyl group, a 4-cyanophenylsulfinyl group, a 4-methoxyphenylsulfinyl group, a 4-methylsulfanylphenylsulfinyl group, a 4-phenylsulfanylphenylsulfinyl group, a 4-dimethylaminophenylsulfinyl group and the like.

As the alkylsulfonyl group which may have a substituent group, an alkylsulfonyl group having from 1 to 20 carbon atoms is preferred, and examples thereof include a methylsulfonyl group, an ethylsulfonyl group, a propylsulfonyl group, an isopropylsulfonyl group, a butylsulfonyl group, a hexylsulfonyl group, a cyclohexylsulfonyl group, an octylsulfonyl group, a 2-ethylhexylsulfonyl group, a decanoylsulfonyl group, a dodecanoylsulfonyl group, an octadecanoylsulfonyl group, a cyanomethylsulfonyl group, a methoxymethylsulfonyl group, a perfluoroalkylsulfonyl group and the like.

As the arylsulfonyl group which may have a substituent group, an arylsulfonyl group having from 6 to 30 carbon atoms is preferred, and examples thereof include a phenylsulfonyl group, a 1-naphthylsulfonyl group, a 2-naphthylsulfonyl group, a 2-chlorophenylsulfonyl group, a 2-methylphenylsulfonyl group, a 2-methoxyphenylsulfonyl group, a 2-butoxyphenylsulfonyl group, a 3-chlorophenylsulfonyl group, a 3-trifluoromethylphenylsulfonyl group, a 3-cyanophenylsulfonyl group, a 3-nitrophenylsulfonyl group, a 4-fluorophenylsulfonyl group, a 4-cyanophenylsulfonyl group, a 4-methoxyphenylsulfonyl group, a 4-methylsulfanylphenylsulfonyl group, a 4-phenylsulfanylphenylsulfonyl group, a 4-dimethylaminophenylsulfonyl group and the like.

As the acyl group which may have a substituent group, an acyl group having from 2 to 20 carbon atoms is preferred, and examples thereof include an acetyl group, a propanoyl group, a butanoyl group, a trifluoromethylcarbonyl group, a pentanoyl group, a benzoyl group, a

1-naphthoyl group, a 2-naphthoyl group, a 4-methylsulfanylbenzoyl group, a 4-phenylsulfanylbenzoyl group, a 4-dimethylaminobenzoyl group, a 4-diethylaminobenzoyl group, a 2-chlorobenzoyl group, a 2-methylbenzoyl group, a 2-methoxybenzoyl group, a 2-butoxybenzoyl group, a 3-chlorobenzoyl group, a 3-trifluoromethylbenzoyl group, a 3-cyanobenzoyl group, a 3-nitrobenzoyl group, a 4-fluorobenzoyl group, a 4-cyanobenzoyl group, a 4-methoxybenzoyl group and the like.

As the alkoxycarbonyl group which may have a substituent group, an alkoxycarbonyl group having from 2 to 20 carbon atoms is preferred, and examples thereof include a methoxycarbonyl group, an ethoxycarbonyl group, a propoxycarbonyl group, a butoxycarbonyl group, a hexyloxycarbonyl group, an octyloxycarbonyl group, a decyloxycarbonyl group, an octadecyloxycarbonyl group, a trifluoromethyloxycarbonyl group and the like.

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

As the phosphinoyl group which may have a substituent group, a phosphinoyl group having from 2 to 50 total carbon atoms is preferred, and examples thereof include a dimethyl phosphinoyl group, a diethylphosphinoyl group, a dipropylphosphinoyl group, a diphenylphosphinoyl group, a dimethoxyphosphinoyl group, a diethoxyphosphinoyl group, a dibenzoylphosphinoyl group, a bis(2,4,6-trimethylphenyl)phosphinoyl group and the like.

As the heterocyclic group which may have a substituent group, an aromatic or aliphatic heterocycle containing a nitrogen atom, an oxygen atom, a sulfur atom, and a phosphorus atom is preferred. Examples thereof include a thienyl group, a benzo[b] thienyl group, a naphtho[2,3-b]thienyl group, a thianthrenyl group, a furyl group, a pyranyl group, an isobenzofuranyl group, a chromenyl group, a xanthenyl group, a phenoxathiinyl group, a 2H-pyrrolyl group, a pyrrolyl group, an imidazolyl group, a pyrazolyl group, a pyridyl group,

a pyrazinyl group, a pyrimidinyl group, a pyridazinyl group, an indolizinyl group, an isoindolyl group, a 3H-indolyl group, an indolyl group, a 1H-indazolyl group, a purinyl group, a 4H-quinolizinyl group, an isoquinolyl group, a quinolyl group, a phthalazinyl group, a naphthyridinyl group, a quinoxalinyl group, a quinazolinyl group, a cinnolinyl group, a pteridinyl group, a 4aH-carbazolyl group, a carbazolyl group, a β -carbolinyl group, a phenanthridinyl group, an acridinyl group, a perimidinyl group, a phenanthrolinyl group, a phenazinyl group, a phenarsazinyl group, an isothiazolyl group, a phenothiazinyl group, an isoxazolyl group, a furazanyl group, a phenoxazinyl group, an isochromanyl group, a chromanyl group, a pyrrolidinyl group, a pyrrolinyl group, an imidazolidinyl group, an imidazolyl group, a pyrazolidinyl group, a pyrazolyl group, a piperidyl group, a piperazinyl group, an indolyl group, an isoindolyl group, a quinuclidinyl group, a morpholinyl group, a thioxantholyl group and the like.

Examples of the alkylthiocarbonyl group which may have a substituent group include a methylthiocarbonyl group, a propylthiocarbonyl group, a butylthiocarbonyl group, a hexylthiocarbonyl group, an octylthiocarbonyl group, a decylthiocarbonyl group, an octadecylthiocarbonyl group, a trifluoromethyl thiocarbonyl group and the like.

Examples of the arylthiocarbonyl group which may have a substituent group include a 1-naphthylthiocarbonyl group, a 2-naphthylthiocarbonyl group, a 4-methylsulfanylphenylthiocarbonyl group, a 4-phenylsulfanylphenylthiocarbonyl group, a 4-dimethylaminophenylthiocarbonyl group, a 4-diethylaminophenylthiocarbonyl group, a 2-chlorophenylthiocarbonyl group, a 2-methylphenylthiocarbonyl group, a 2-methoxyphenylthiocarbonyl group, a 2-butoxyphenylthiocarbonyl group, a 3-chlorophenylthiocarbonyl group, a 3-trifluoromethylphenylthiocarbonyl group, a 3-cyanophenylthiocarbonyl group, a 3-nitrophenylthiocarbonyl group, a 4-fluorophenylthiocarbonyl group, a 4-cyanophenylthiocarbonyl group, a 4-methoxyphenylthiocarbonyl group and the like.

Examples of the dialkylaminocarbonyl group which may have a substituent group include a dimethylaminocarbonyl group, a diethylaminocarbonyl group, a dipropylaminocarbonyl group, a dibutylaminocarbonyl group and the like.

Examples of the dialkylaminothiocarbonyl group which may have a substituent group include a dimethylaminothiocarbonyl group, a dipropylaminothiocarbonyl group, a dibutylaminothiocarbonyl group and the like.

Among them, from the viewpoint of increasing the sensitivity, R in formula (a) is more

preferably an acyl group, and specifically, an acetyl group, an ethyloyl group, a propioyl group, a benzoyl group and a tolyl group are preferred.

Examples of the divalent organic group represented by A in formula (a) include alkylene having from 1 to 12 carbon atoms, which may have a substituent group, cyclohexylene which may have a substituent group, and alkynylene which may have a substituent group.

Examples of substituent groups that may be introduced into these groups include a halogen group such as a fluorine atom, a chlorine atom, a bromine atom and an iodine atom, an alkoxy group such as a methoxy group, an ethoxy group and a tert-butoxy group, an aryloxy group such as a phenoxy group and a p-tolyloxy group, an alkoxycarbonyl group such as a methoxycarbonyl group, a butoxycarbonyl group and a phenoxycarbonyl group, an acyloxy group such as an acetoxyl group, a propionyloxy group and a benzoyloxy group, an acyl group such as an acetyl group, a benzoyl group, an isobutylyl group, an acryloyl group, a methacryloyl group and a methoxalyl group, an alkylsulfanyl group such as a methylsulfanyl group and a tert-butylsulfanyl group, an arylsulfanyl group such as a phenylsulfanyl group and a p-tolylsulfanyl group, an alkylamino group such as a methylamino group and a cyclohexylamino group, a dialkylamino group such as a dimethylamino group, a diethylamino group, a morpholino group and a piperidino group, an arylamino group such as a phenylamino group and a p-tolylamino group, an alkyl group such as a methyl group, an ethyl group, a tert-butyl group and a dodecyl group, an aryl group such as a phenyl group, a p-tolyl group, a xylyl group, a cumenyl group, a naphthyl group, an anthryl group and a phenanthryl group, and other groups such as a hydroxyl group, a carboxyl group, a formyl group, a mercapto group, a sulfo group, a mesyl group, a p-toluene sulfonyl group, an amino group, a nitro group, a cyano group, a trifluoromethyl group, a trichloromethyl group, a trimethylsilyl group, a phosphinico group, a phosphono group, a trimethylammoniumyl group, a dimethylsulfoniumyl group and a triphenylphenacylphosphoniumyl group.

Among them, from the viewpoint of increasing the sensitivity to suppress the coloration as the heating time passes, A in formula (a) is preferably an unsubstituted alkylene group, an alkylene group substituted with an alkyl group (for example, a methyl group, an ethyl group, a tert-butyl group and a dodecyl group), an alkylene group substituted with an alkenyl group (for example, a vinyl group and an allyl group), and an alkylene group substituted with an aryl group (for example, a phenyl group, a p-tolyl group, a xylyl group, a cumenyl group, a naphthyl group, an anthryl group, a phenanthryl group and a styryl group).

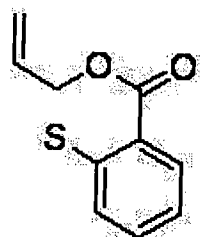
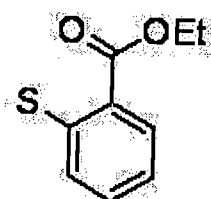
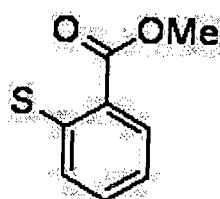
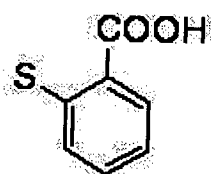
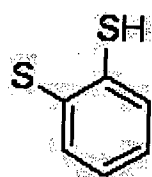
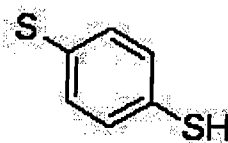
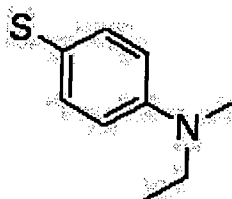
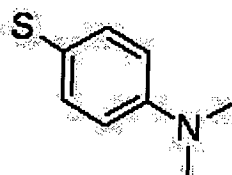
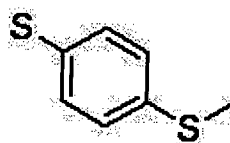
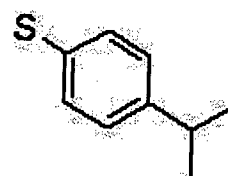
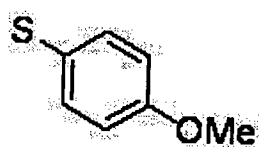
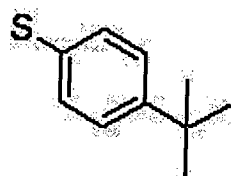
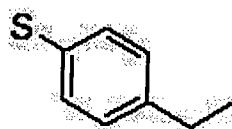
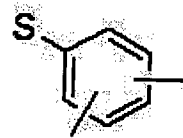
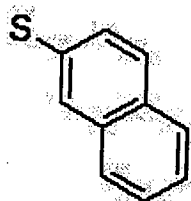
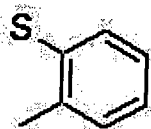
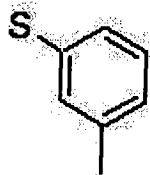
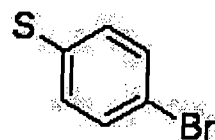
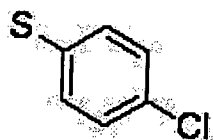
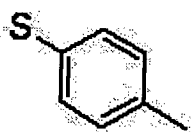
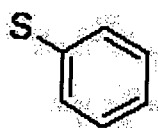
The aryl group represented by Ar in formula (a) is preferably an aryl group having from 6 to 30 carbon atoms, and may have a substituent group.

Specific examples thereof include a phenyl group, a biphenyl group, a 1-naphthyl group, a 2-naphthyl group, a 9-anthryl group, a 9-phenanthryl group, a 1-pyrenyl group, a 5-naphthacenyl group, a 1-indenyl group, a 2-azulenyl group, a 9-fluorenyl group, a terphenyl group, a quarter phenyl group, an o-, m-, and p-tolyl group, a xylyl group, an o-, m-, and p-cumenyl group, a mesityl group, a pentalenyl group, a binaphthalenyl group, ternaphthalenyl group, a quarter naphthalenyl group, a heptalenyl group, a biphenylenyl group, an indacenyl group, a fluoranthenyl group, an acenaphthylenyl group, an aceanthrylenyl group, a phenalenyl group, a fluorenyl group, an anthryl group, a bianthracenyl group, a teranthracenyl group, a quarter anthracenyl group, an anthraquinolyl group, a phenanthryl group, a triphenylenyl group, a pyrenyl group, a chrysenyl group, a naphthacenyl group, a pleiadenyl group, a picenyl group, a perylenyl group, a pentaphenyl group, a pentacenyl group, a tetraphenylenyl group, a hexaphenyl group, a hexacenyl group, a rubicenyl group, a coronenyl group, a trinaphthylenyl group, a heptaphenyl group, a heptacenyl group, a pyranthrenyl group, an ovalenyl group and the like. Among them, from the viewpoint of increasing the sensitivity to suppress the coloration as the heating time passes, a substituted or unsubstituted phenyl group is preferred.

When the phenyl group has a substituent group, examples of the substituent group include a halogen group such as a fluorine atom, a chlorine atom, a bromine atom and an iodine atom, an alkoxy group such as a methoxy group, an ethoxy group and a tert-butoxy group, an aryloxy group such as a phenoxy group and a p-tolyloxy group, an alkylthio group such as a methylthio group, an ethylthio group and a tert-butylthio group, an arylthio group such as a phenylthio group and a p-tolylthio group, an alkoxycarbonyl group such as a methoxycarbonyl group, a butoxycarbonyl group and a phenoxycarbonyl group, an acyloxy group such as an acetoxy group, a propionyloxy group and a benzoyloxy group, an acyl group such as an acetyl group, a benzoyl group, an isobutylyl group, an acryloyl group, a methacryloyl group and a methoxalyl group, an alkylsulfanyl group such as a methylsulfanyl group and a tert-butylsulfanyl group, an arylsulfanyl group such as a phenylsulfanyl group and a p-tolylsulfanyl group, an alkylamino group such as a methylamino group and a cyclohexylamino group, a dialkylamino group such as a dimethylamino group, a diethylamino group, a morpholino group and a piperidino group, an arylamino group such as a phenylamino group and a p-tolylamino group, an alkyl group such as an ethyl group, a tert-butyl group and

a dodecyl group, and a hydroxyl group, a carboxyl group, a formyl group, a mercapto group, a sulfo group, a mesyl group, a p-toluene sulfonyl group, an amino group, a nitro group, a cyano group, a trifluoromethyl group, a trichloromethyl group, a trimethylsilyl group, a phosphinico group, a phosphono group, a trimethylammoniumyl group, a dimethylsulfoniumyl group, a triphenyl phenacylphosphoniumyl group and the like.

In formula (a), from the viewpoint of the sensitivity, it is preferred that the structure of "SAr" formed by Ar and S adjacent to the Ar is any the structure shown below.



Examples of the monovalent substituent group represented by X in formula (a) include an alkyl group which may have a substituent group, an aryl group which may have a substituent group, an alkenyl group which may have a substituent group, an alkynyl group which may have a substituent group, an alkoxy group which may have a substituent group, an aryloxy group which may have a substituent group, an alkylthio group which may have a substituent group, an arylthio group which may have a substituent group, an acyloxy group which may have a substituent group, an alkylsulfanyl group which may have a substituent group, an arylsulfanyl group which may have a substituent group, an alkylsulfinyl group which may have a substituent group, an arylsulfinyl group which may have a substituent group, an alkylsulfonyl group which may have a substituent group, an arylsulfonyl group which may have a substituent group, an acyl group which may have a substituent group, an alkoxycarbonyl group which may have a substituent group, a carbamoyl group which may have a substituent group, a sulfamoyl group which may have a substituent group, an amino group which may have a substituent group, a phosphinoyl group which may have a substituent group, a heterocyclic group which may have a substituent group, a halogen group, and the like.

As the alkyl group which may have a substituent group, an alkyl group having from 1 to 30 carbon atoms is preferred, and examples thereof include a methyl group, an ethyl group, a propyl group, a butyl group, a hexyl group, an octyl group, a decyl group, a dodecyl group, an octadecyl group, an isopropyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, a 1-ethylpentyl group, a cyclopentyl group, a cyclohexyl group, a trifluoromethyl group, a 2-ethylhexyl group, a phenacyl group, a 1-naphthoylmethyl group, a 2-naphthoylmethyl group, a 4-methylsulfanylphenacyl group, a 4-phenylsulfanylphenacyl group, a 4-dimethylaminophenacyl group, a 4-cyanophenacyl group, a 4-methylphenacyl group, a 2-methylphenacyl group, a 3-fluorophenacyl group, a 3-trifluoromethylphenacyl group, 3-nitrophenacyl group and the like.

As the aryl group which may have a substituent group, an aryl group having from 6 to 30 carbon atoms is preferred, and examples thereof include a phenyl group, a biphenyl group, a 1-naphthyl group, a 2-naphthyl group, a 9-anthryl group, a 9-phenanthryl group, a 1-pyrenyl group, a 5-naphthacenyl group, a 1-indenyl group, a 2-azulenyl group, a 9-fluorenyl group, a terphenyl group, a quarter phenyl group, an o-, m-, and p-tolyl group, a xylyl group, an o-, m-, and p-cumenyl group, a mesityl group, a pentalenyl group, a binaphthalenyl group, a ternaphthalenyl group, a quarter naphthalenyl group, a heptalenyl group, a biphenylenyl group, an indacenyl group, a fluoranthenyl group, an acenaphthylenyl group, an aceanthrylenyl group,

a phenalenyl group, a fluorenyl group, an anthryl group, a bianthracenyl group, a teranthracenyl group, a quarter anthracenyl group, an anthraquinolyl group, a phenanthryl group, a triphenylenyl group, a pyrenyl group, a chrysenyl group, a naphthacenyl group, a pleiadenyl group, a picenyl group, a perylenyl group, a pentaphenyl group, a pentacenyl group, a tetraphenylenyl group, a hexaphenyl group, a hexacenyl group, a rubicenyl group, a coronenyl group, a trinaphthylenyl group, a heptaphenyl group, a heptacenyl group, a pyranthrenyl group, an ovalenyl group and the like.

As the alkenyl group which may have a substituent group, an alkenyl group having from 2 to 10 carbon atoms is preferred, and examples thereof include a vinyl group, an allyl group, a styryl group and the like.

As the alkynyl group which may have a substituent group, an alkynyl group having from 2 to 10 carbon atoms is preferred, and examples thereof include an ethynyl group, a propynyl group, a propargyl group and the like.

As the alkoxy group which may have a substituent group, an alkoxy group having from 1 to 30 carbon atoms is preferred, and examples thereof include a methoxy group, an ethoxy group, a propyloxy group, an isopropyloxy group, a butoxy group, an isobutoxy group, a sec-butoxy group, a tert-butoxy group, a pentyloxy group, an isopentyloxy group, a hexyloxy group, a heptyloxy group, an octyloxy group, a 2-ethylhexyloxy group, a decyloxy group, a dodecyloxy group, an octadecyloxy group, an ethoxycarbonylmethyl group, a 2-ethylhexyloxycarbonyl methyloxy group, an aminocarbonylmethyloxy group, an N,N-dibutylaminocarbonylmethyloxy group, an N-methylaminocarbonylmethyloxy group, an N-ethylaminocarbonylmethyloxy group, an N-octylaminocarbonylmethyloxy group, an N-methyl-N-benzylaminocarbonylmethyloxy group, a benzyloxy group, a cyanomethyloxy group and the like.

As the aryloxy group which may have a substituent group, an aryloxy group having from 6 to 30 carbon atoms is preferred, and examples thereof include a phenyloxy group, a 1-naphthyloxy group, a 2-naphthyloxy group, a 2-chlorophenyloxy group, a 2-methylphenyloxy group, a 2-methoxyphenyloxy group, a 2-butoxyphenyloxy group, a 3-chlorophenyloxy group, a 3-trifluoromethylphenyloxy group, a 3-cyanophenyloxy group, a 3-nitrophenyloxy group, a 4-fluorophenyloxy group, a 4-cyanophenyloxy group, a 4-methoxy phenyloxy group, a 4-dimethylaminophenyloxy group, a 4-methylsulfanylphenyloxy group, a 4-phenylsulfanylphenyloxy group and the like.

As the alkylthio group which may have a substituent group, a thioalkoxy group having

from 1 to 30 carbon atoms is preferred, and examples thereof include a methylthio group, an ethylthio group, a propylthio group, an isopropylthio group, a butylthio group, an isobutylthio group, a sec-butylthio group, a tert-butylthio group, a pentylthio group, an isopentylthio group, a hexylthio group, a heptylthio group, an octylthio group, a 2-ethylhexylthio group, a decylthio group, a dodecylthio group, an octadecylthio group, a benzylthio group and the like.

As the arylthio group which may have a substituent group, an arylthio group having from 6 to 30 carbon atoms is preferred, and examples thereof include a phenylthio group, a 1-naphthylthio group, a 2-naphthylthio group, a 2-chlorophenylthio group, a 2-methylphenylthio group, a 2-methoxyphenylthio group, a 2-butoxyphenylthio group, a 3-chlorophenylthio group, a 3-trifluoromethylphenylthio group, a 3-cyanophenylthio group, a 3-nitrophenylthio group, a 4-fluorophenylthio group, a 4-cyanophenylthio group, a 4-methoxyphenylthio group, a 4-dimethylaminophenylthio group, a 4-methylsulfanylphenylthio group, a 4-phenylsulfanylphenylthio group and the like.

As the acyloxy group which may have a substituent group, an acyloxy group having from 2 to 20 carbon atoms is preferred, and examples thereof include an acetyloxy group, a propanoyloxy group, a butanoyloxy group, a pentanoyloxy group, a trifluoromethylcarbonyloxy group, a benzoyloxy group, a 1-naphthylcarbonyloxy group, a 2-naphthylcarbonyloxy group and the like.

As the alkylsulfanyl group which may have a substituent group, an alkylsulfanyl group having from 1 to 20 carbon atoms is preferred, and examples thereof include a methylsulfanyl group, an ethylsulfanyl group, a propylsulfanyl group, an isopropylsulfanyl group, a butylsulfanyl group, a hexylsulfanyl group, a cyclohexylsulfanyl group, an octylsulfanyl group, a 2-ethylhexylsulfanyl group, a decanoylsulfanyl group, a dodecanoylsulfanyl group, an octadecanoylsulfanyl group, a cyanomethylsulfanyl group, a methoxymethylsulfanyl group and the like.

As the arylsulfanyl group which may have a substituent group, an arylsulfanyl group having from 6 to 30 carbon atoms is preferred, and examples thereof include a phenylsulfanyl group, a 1-naphthylsulfanyl group, a 2-naphthylsulfanyl group, a 2-chlorophenylsulfanyl group, a 2-methylphenylsulfanyl group, a 2-methoxyphenylsulfanyl group, a 2-butoxyphenylsulfanyl group, a 3-chlorophenylsulfanyl group, a 3-trifluoromethylphenylsulfanyl group, a 3-cyanophenylsulfanyl group, a 3-nitrophenylsulfanyl group, a 4-fluorophenylsulfanyl group, a 4-cyanophenylsulfanyl group, a 4-methoxyphenylsulfanyl group, a 4-methylsulfanylphenylsulfanyl group, a

4-phenylsulfanylyphenylsulfanyl group, a 4-dimethylaminophenylsulfanyl group and the like.

As the alkylsulfanyl group which may have a substituent group, an alkylsulfanyl group having from 1 to 20 carbon atoms is preferred, and examples thereof include a methylsulfanyl group, an ethylsulfanyl group, a propylsulfanyl group, an isopropylsulfanyl group, a butylsulfanyl group, a hexylsulfanyl group, a cyclohexylsulfanyl group, an octylsulfanyl group, a 2-ethylhexylsulfanyl group, a decanoylsulfanyl group, a dodecanoylsulfanyl group, an octadecanoylsulfanyl group, a cyanomethylsulfanyl group, a methoxymethylsulfanyl group and the like.

As the arylsulfanyl group which may have a substituent group, an arylsulfanyl group having from 6 to 30 carbon atoms is preferred, and examples thereof include a phenylsulfanyl group, a 1-naphthylsulfanyl group, a 2-naphthylsulfanyl group, a 2-chlorophenylsulfanyl group, a 2-methylphenylsulfanyl group, a 2-methoxyphenylsulfanyl group, a 2-butoxyphenylsulfanyl group, a 3-chlorophenylsulfanyl group, a 3-trifluoromethylphenylsulfanyl group, a 3-cyanophenylsulfanyl group, a 3-nitrophenylsulfanyl group, a 4-fluorophenylsulfanyl group, a 4-cyanophenylsulfanyl group, a 4-methoxyphenylsulfanyl group, a 4-methylsulfanylyphenylsulfanyl group, a 4-phenylsulfanylyphenylsulfanyl group, a 4-dimethylaminophenylsulfanyl group and the like.

As the alkylsulfonyl group which may have a substituent group, an alkylsulfonyl group having from 1 to 20 carbon atoms is preferred, and examples thereof include a methylsulfonyl group, an ethylsulfonyl group, a propylsulfonyl group, an isopropylsulfonyl group, a butylsulfonyl group, a hexylsulfonyl group, a cyclohexylsulfonyl group, an octylsulfonyl group, a 2-ethylhexylsulfonyl group, a decanoylsulfonyl group, a dodecanoylsulfonyl group, an octadecanoylsulfonyl group, a cyanomethylsulfonyl group, a methoxymethylsulfonyl group and the like.

As the arylsulfonyl group which may have a substituent group, an arylsulfonyl group having from 6 to 30 carbon atoms is preferred, and examples thereof include a phenylsulfonyl group, a 1-naphthylsulfonyl group, a 2-naphthylsulfonyl group, a 2-chlorophenylsulfonyl group, a 2-methylphenylsulfonyl group, a 2-methoxyphenylsulfonyl group, a 2-butoxyphenylsulfonyl group, a 3-chlorophenylsulfonyl group, a 3-trifluoromethylphenylsulfonyl group, a 3-cyanophenylsulfonyl group, a 3-nitrophenylsulfonyl group, a 4-fluorophenylsulfonyl group, a 4-cyanophenylsulfonyl group, a 4-methoxyphenylsulfonyl group, a 4-methylsulfanylyphenylsulfonyl group, a 4-phenylsulfanylyphenylsulfonyl group, a 4-dimethylaminophenylsulfonyl group and the like.

As the acyl group which may have a substituent group, an acyl group having from 2 to 20 carbon atoms is preferred, and examples thereof include an acetyl group, a propanoyl group, a butanoyl group, a trifluoromethylcarbonyl group, a pentanoyl group, a benzoyl group, a 1-naphthoyl group, a 2-naphthoyl group, a 4-methylsulfanylbzoyl group, a 4-phenylsulfanylbzoyl group, a 4-dimethylaminobzoyl group, a 4-diethylaminobzoyl group, a 2-chlorobzoyl group, a 2-methylbzoyl group, a 2-methoxybzoyl group, a 2-butoxybzoyl group, a 3-chlorobzoyl group, a 3-trifluoromethylbzoyl group, a 3-cyanobzoyl group, a 3-nitrobzoyl group, a 4-fluorobzoyl group, a 4-cyanobzoyl group, a 4-methoxybzoyl group and the like.

As the alkoxycarbonyl group which may have a substituent group, an alkoxycarbonyl group having from 2 to 20 carbon atoms is preferred, and examples thereof include a methoxycarbonyl group, an ethoxycarbonyl group, a propoxycarbonyl group, a butoxycarbonyl group, a hexyloxycarbonyl group, an octyloxycarbonyl group, a decyloxycarbonyl group, an octadecyloxycarbonyl group, a phenoxycarbonyl group, a trifluoromethyloxycarbonyl group, a 1-naphthyloxycarbonyl group, a 2-naphthyloxycarbonyl group, a 4-methylsulfanylphenyloxycarbonyl group, a 4-phenylsulfanylphenyloxycarbonyl group, a 4-dimethylaminophenyloxycarbonyl group, a 4-diethylaminophenyloxycarbonyl group, a 2-chlorophenyloxycarbonyl group, a 2-methylphenyloxycarbonyl group, a 2-methoxyphenyloxycarbonyl group, a 2-butoxyphenyloxycarbonyl group, a 3-chlorophenyloxycarbonyl group, a 3-trifluoromethylphenyloxycarbonyl group, a 3-cyanophenyloxycarbonyl group, a 3-nitrophenyloxycarbonyl group, a 4-fluorophenyloxycarbonyl group, a 4-cyanophenyloxycarbonyl group, 4-methoxyphenyloxycarbonyl group and the like.

As the carbamoyl group which may have a substituent group, a carbamoyl group having from 1 to 30 total carbon atoms is preferred, and examples thereof include an N-methylcarbamoyl group, an N-ethylcarbamoyl group, an N-propylcarbamoyl group, an N-butylcarbamoyl group, an N-hexylcarbamoyl group, an N-cyclohexylcarbamoyl group, an N-octylcarbamoyl group, an N-decylcarbamoyl group, an N-octadecylcarbamoyl group, an N-phenylcarbamoyl group, an N-2-methylphenylcarbamoyl group, an N-2-chlorophenylcarbamoyl group, an N-2-isopropoxyphenylcarbamoyl group, an N-2-(2-ethylhexyl)phenylcarbamoyl group, an N-3-chlorophenylcarbamoyl group, an N-3-nitrophenylcarbamoyl group, an N-3-cyanophenylcarbamoyl group, an N-4-methoxyphenylcarbamoyl group, an N-4-cyanophenylcarbamoyl group, an

N-4-methylsulfanylyphenylcarbamoyl group, an N-4-phenylsulfanylyphenylcarbamoyl group, an N-methyl-N-phenylcarbamoyl group, an N,N-dimethylcarbamoyl group, an N,N-dibutylcarbamoyl group, an N,N-diphenylcarbamoyl group and the like.

As the sulfamoyl group which may have a substituent group, a sulfamoyl group having from 0 to 30 total carbon atoms is preferred, and examples thereof include a sulfamoyl group, an N-alkylsulfamoyl group, an N-arylsulfamoyl group, an N,N-dialkylsulfamoyl group, an N,N-diarylsulfamoyl group, an N-alkyl-N-arylsulfamoyl group, and the like. More specific examples thereof include an N-methylsulfamoyl group, an N-ethylsulfamoyl group, an N-propylsulfamoyl group, an N-butylsulfamoyl group, an N-hexylsulfamoyl group, an N-cyclohexylsulfamoyl group, an N-octylsulfamoyl group, an N-2-ethylhexylsulfamoyl group, an N-decylsulfamoyl group, an N-octadecylsulfamoyl group, an N-phenylsulfamoyl group, an N-2-methylphenylsulfamoyl group, an N-2-chlorophenylsulfamoyl group, an N-2-methoxyphenylsulfamoyl group, an N-2-isopropoxyphenylsulfamoyl group, an N-3-chlorophenylsulfamoyl group, an N-3-nitrophenylsulfamoyl group, an N-3-cyanophenylsulfamoyl group, an N-4-methoxyphenylsulfamoyl group, an N-4-cyanophenylsulfamoyl group, an N-4-dimethylaminophenylsulfamoyl group, an N-4-methylsulfanylyphenylsulfamoyl group, an N-4-phenylsulfanylyphenylsulfamoyl group, an N-methyl-N-phenylsulfamoyl group, an N,N-dimethylsulfamoyl group, an N,N-dibutylsulfamoyl group, an N,N-diphenylsulfamoyl group and the like.

As the amino group which may have a substituent group, an amino group having from 0 to 50 total carbon atoms is preferred, and examples thereof include -NH₂, an N-alkylamino group, an N-arylamino group, an N-acylamino group, an N-sulfonylamino group, an N,N-dialkylamino group, an N,N-diarylamino group, an N-alkyl-N-arylamino group, an N,N-disulfonylamino group, and the like. More specific examples thereof include an N-methylamino group, an N-ethylamino group, an N-propylamino group, an N-isopropylamino group, an N-butylamino group, an N-tert-butylamino group, an N-hexylamino group, an N-cyclohexylamino group, an N-octylamino group, an N-2-ethylhexylamino group, an N-decylamino group, an N-octadecylamino group, an N-benzylamino group, an N-phenylamino group, an N-2-methylphenylamino group, an N-2-chlorophenylamino group, an N-2-methoxyphenylamino group, an N-2-isopropoxyphenylamino group, an N-2-(2-ethylhexyl)phenylamino group, an N-3-chlorophenylamino group, an N-3-nitrophenylamino group, an N-3-cyanophenylamino group, an N-3-trifluoromethylphenylamino group, an N-4-methoxyphenylamino group, an

N-4-cyanophenylamino group, an N-4-trifluoromethylphenylamino group, an N-4-methylsulfanylphenylamino group, an N-4-phenylsulfanylphenylamino group, an N-4-dimethylaminophenylamino group, an N-methyl-N-phenylamino group, an N,N-dimethylamino group, an N,N-diethylamino group, an N,N-dibutylamino group, an N,N-diphenylamino group, an N,N-diacetylamino group, an N,N-dibenzoylamino group, an N,N-(dibutylcarbonyl)amino group, an N,N-(dimethylsulfonyl)amino group, an N,N-(diethylsulfonyl)amino group, an N,N-(dibutylsulfonyl)amino group, an N,N-(diphenylsulfonyl)amino group, a morpholino group, a 3,5-dimethylmorpholino group, a carbazole group and the like.

As the phosphinoyl group which may have a substituent group, a phosphinoyl group having from 2 to 50 total carbon atoms is preferred, and examples thereof include a dimethyl phosphinoyl group, a diethylphosphinoyl group, a dipropylphosphinoyl group, a diphenylphosphinoyl group, a dimethoxyphosphinoyl group, a diethoxyphosphinoyl group, a dibenzoylphosphinoyl group, a bis(2,4,6-trimethylphenyl)phosphinoyl group and the like.

As the heterocyclic group which may have a substituent group, an aromatic or aliphatic heterocycle containing a nitrogen atom, an oxygen atom, a sulfur atom, and a phosphorus atom is preferred. Examples thereof include a thienyl group, a benzo[b] thienyl group, a naphtho[2,3-b]thienyl group, a thianthrenyl group, a furyl group, a pyranlyl group, an isobenzofuranyl group, a chromenyl group, a xanthenyl group, a phenoxathiinyl group, a 2H-pyrrolyl group, a pyrrolyl group, an imidazolyl group, a pyrazolyl group, a pyridyl group, a pyrazinyl group, a pyrimidinyl group, a pyridazinyl group, an indolizinyll group, an isoindolyl group, a 3H-indolyl group, an indolyl group, a 1H-indazolyl group, a purinyl group, a 4H-quinolizinyll group, an isoquinolyl group, a quinolyl group, a phthalazinyl group, a naphthyridinyl group, a quinoxalinyl group, a quinazolinyl group, a cinnolinyl group, a pteridinyl group, a 4aH-carbazolyl group, a carbazolyl group, a β -carbolinyl group, a phenanthridinyl group, an acridinyl group, a perimidinyl group, a phenanthrolinyl group, a phenazinyl group, a phenarsazinyl group, an isothiazolyl group, a phenothiazinyl group, an isoxazolyl group, a furazanyl group, a phenoxazinyl group, an isochromanyl group, a chromanyl group, a pyrrolidinyl group, a pyrrolinyl group, an imidazolidinyl group, an imidazolinyll group, a pyrazolidinyl group, a pyrazolinyl group, a piperidyl group, a piperazinyl group, an indolinyl group, an isoindolinyl group, a quinuclidinyl group, a morpholinyl group, a thioxantholyl group and the like.

Examples of the halogen groups include a fluorine atom, a chlorine atom, a bromine

atom, an iodine atom, and the like.

An alkyl group which may have a substituent group, an aryl group which may have a substituent group, an alkenyl group which may have a substituent group, an alkynyl group which may have a substituent group, an alkoxy group which may have a substituent group, an aryloxy group which may have a substituent group, an alkylthio group which may have a substituent group, an arylthio group which may have a substituent group, an acyloxy group which may have a substituent group, an alkylsulfanyl group which may have a substituent group, an arylsulfanyl group which may have a substituent group, an alkylsulfinyl group which may have a substituent group, an arylsulfinyl group which may have a substituent group, an alkylsulfonyl group which may have a substituent group, an arylsulfonyl group which may have a substituent group, an acyl group which may have a substituent group, an alkoxycarbonyl group which may have a substituent group, a carbamoyl group which may have a substituent group, a sulfamoyl group which may have a substituent group, an amino group which may have a substituent group, and a heterocyclic group which may have a substituent group may be substituted with another substituent group, which are described above.

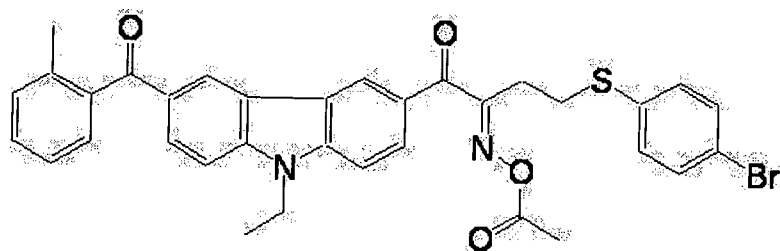
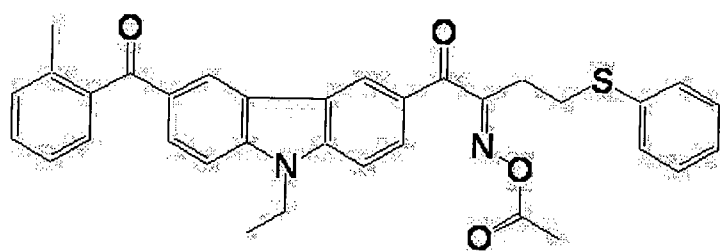
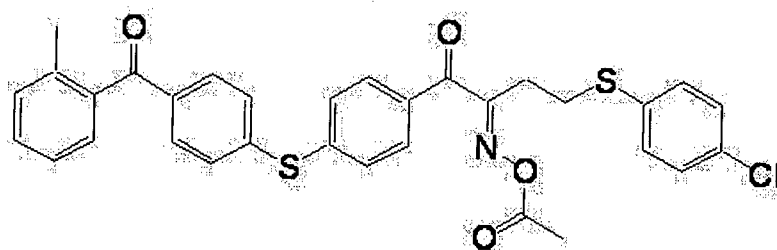
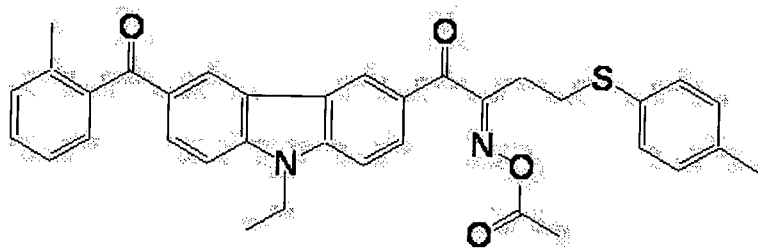
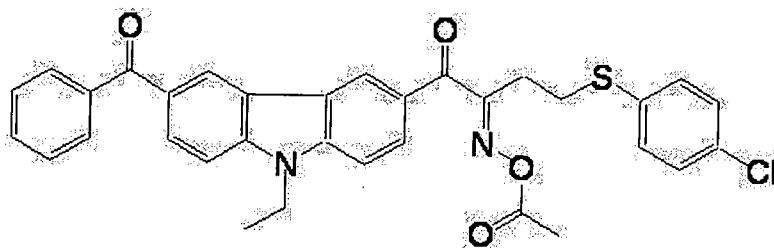
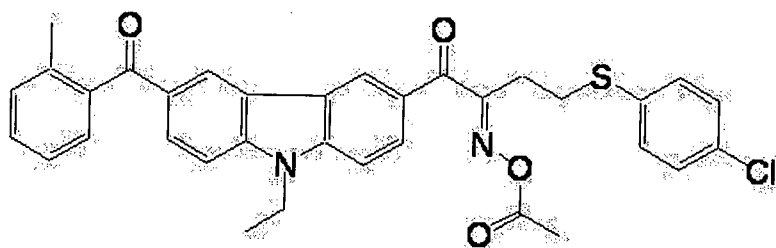
Examples of such substituent groups include a halogen group such as a fluorine atom, a chlorine atom, a bromine atom and an iodine atom, an alkoxy group such as a methoxy group, an ethoxy group and a tert-butoxy group, an aryloxy group such as a phenoxy group and a p-tolyloxy group, an alkoxycarbonyl group such as a methoxycarbonyl group, a butoxycarbonyl group and a phenoxycarbonyl group, an acyloxy group such as an acetoxy group, a propionyloxy group and a benzoyloxy group, an acyl group such as an acetyl group, a benzoyl group, an isobutylyl group, an acryloyl group, a methacryloyl group and a methoxalyl group, an alkylsulfanyl group such as a methylsulfanyl group and a tert-butylsulfanyl group, an arylsulfanyl group such as a phenylsulfanyl group and a p-tolylsulfanyl group, an alkylamino group such as a methylamino group and a cyclohexylamino group, a dialkylamino group such as a dimethylamino group, a diethylamino group, a morpholino group and a piperidino group, an arylamino group such as a phenylamino group and a p-tolylamino group, an alkyl group such as a methyl group, an ethyl group, a tert-butyl group and a dodecyl group, an aryl group such as a phenyl group, a p-tolyl group, a xylyl group, a cumenyl group, a naphthyl group, an anthryl group and a phenanthryl group, and other groups such as a hydroxyl group, a carboxyl group, a formyl group, a mercapto group, a sulfo group, a mesyl group, a p-toluene sulfonyl group, an amino group, a nitro group, a cyano group, a

trifluoromethyl group, a trichloromethyl group, a trimethylsilyl group, a phosphinico group, a phosphono group, a trimethylammoniumyl group, a dimethylsulfoniumyl group and a triphenylphenacylphosphoniumyl group.

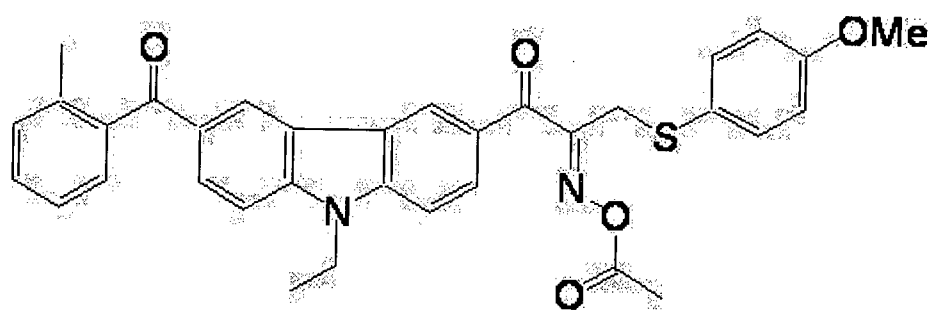
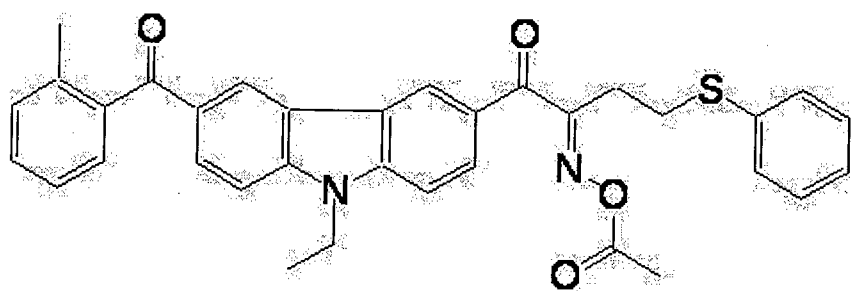
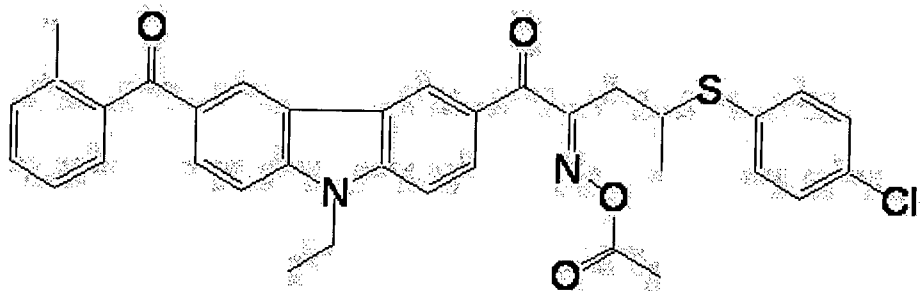
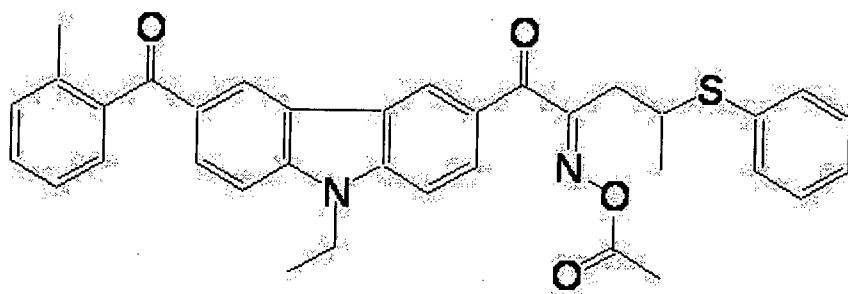
Among them, from the viewpoint of increasing solubility in a solvent and increasing absorption efficiency in a long wavelength region, X in formula (a) is preferably an alkyl group which may have a substituent group, an aryl group which may have a substituent group, an alkenyl group which may have a substituent group, an alkynyl group which may have a substituent group, an alkoxy group which may have a substituent group, an aryloxy group which may have a substituent group, an alkylthio group which may have a substituent group, an arylthio group which may have a substituent group, and an amino group which may have a substituent group.

In formula (a), n represents an integer of from 0 to 5, and preferably an integer of from 0 to 2.

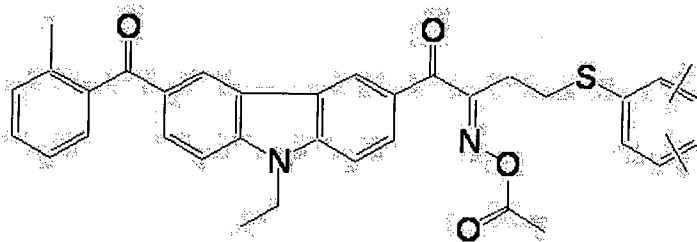
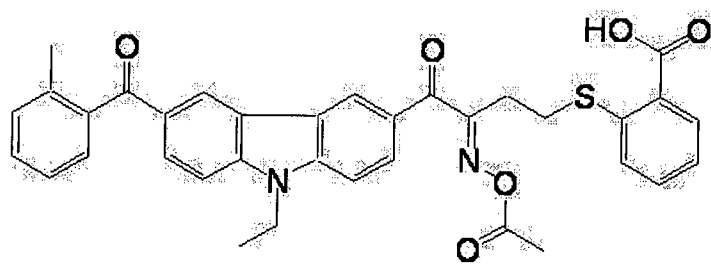
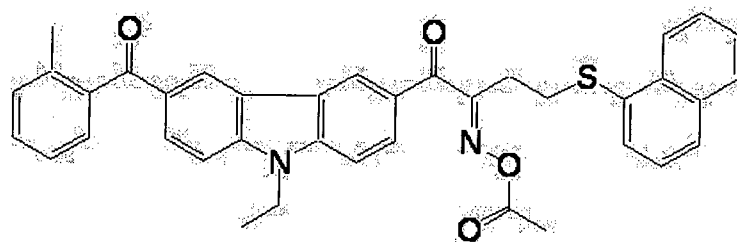
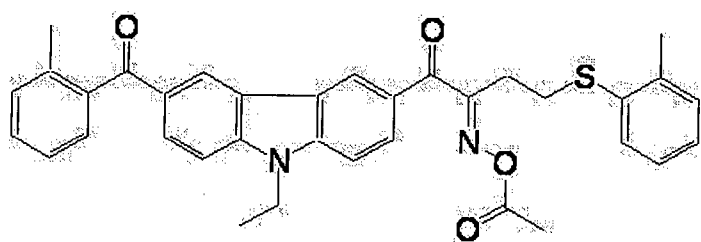
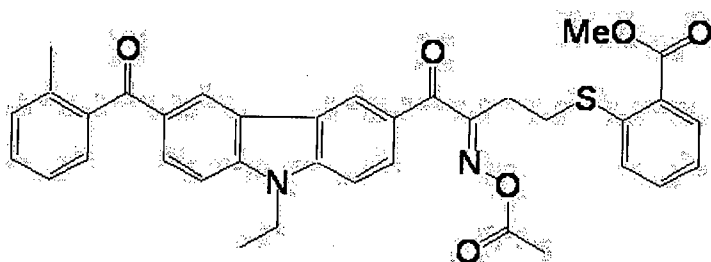
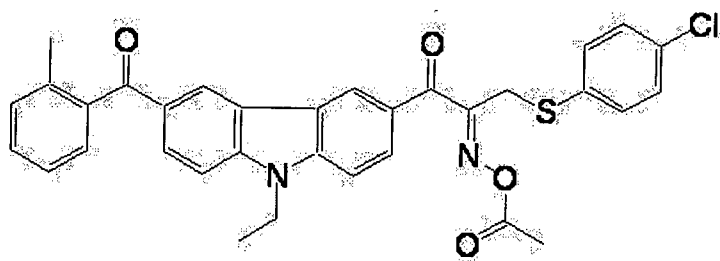
Hereinafter, specific examples of oxime compounds will be shown, but the present invention is not limited thereto.



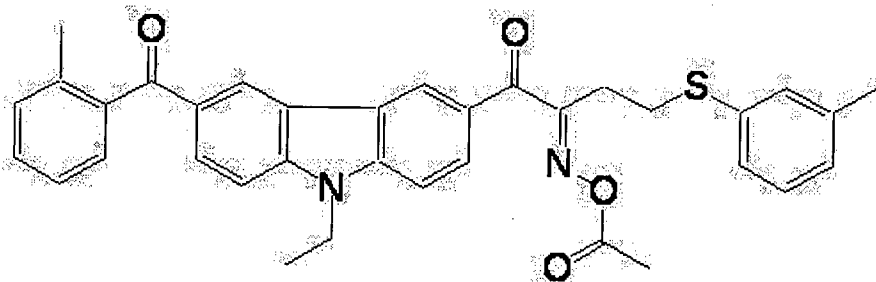
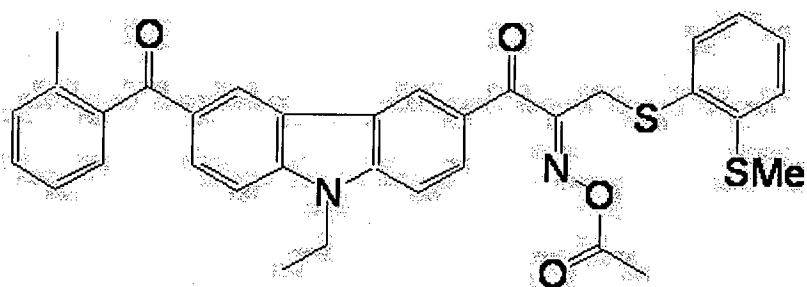
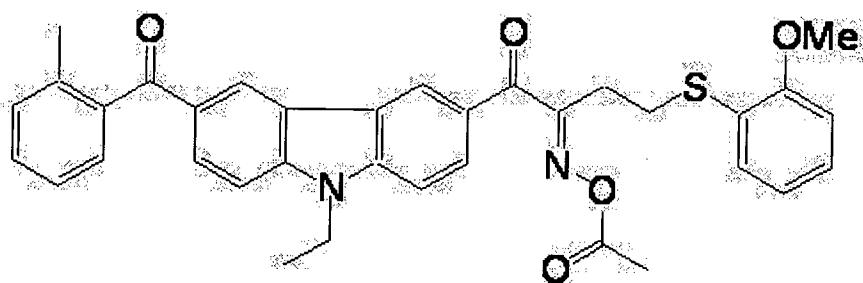
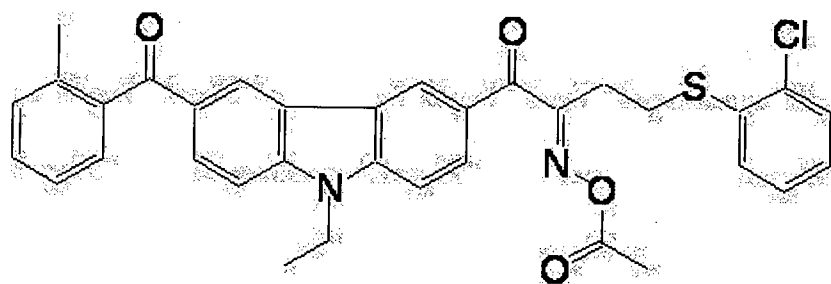
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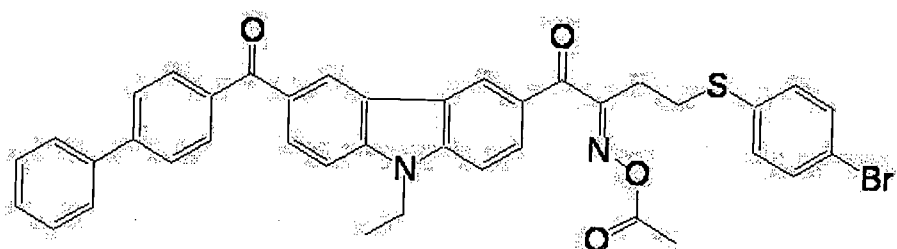
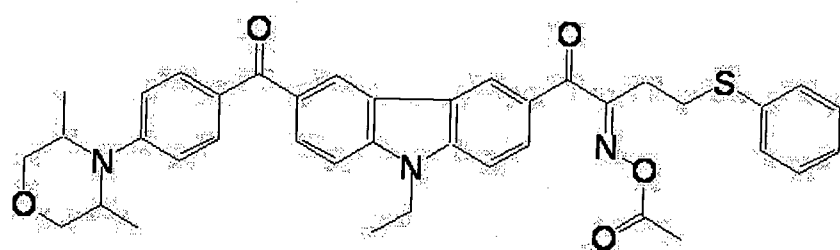
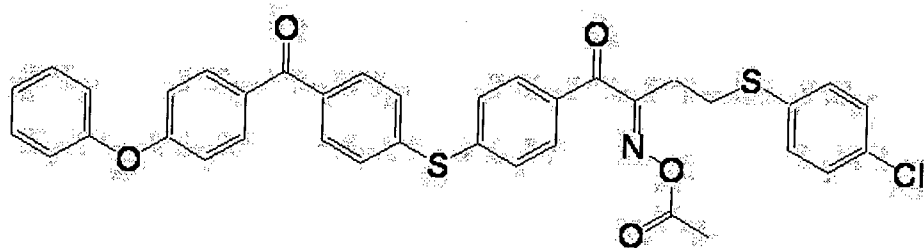
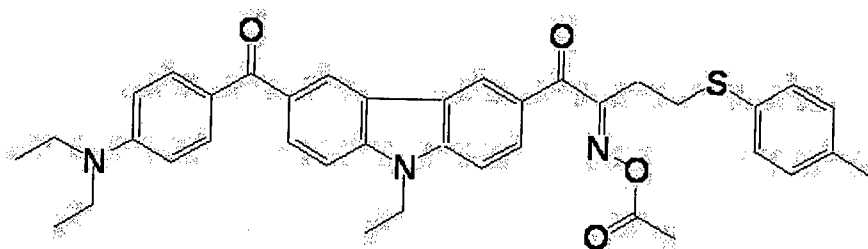
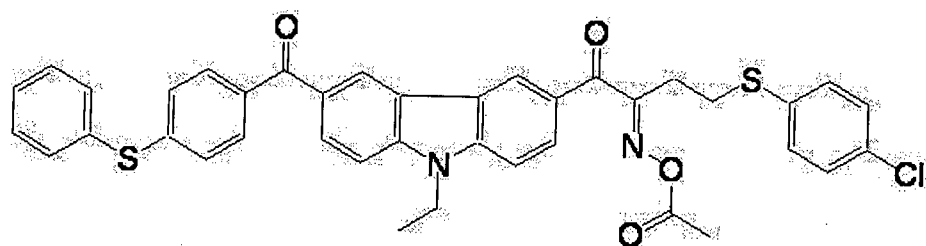
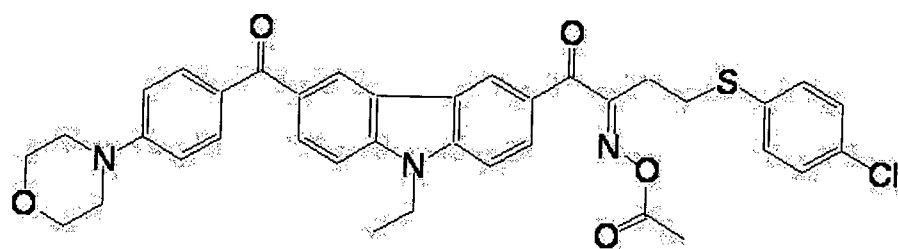
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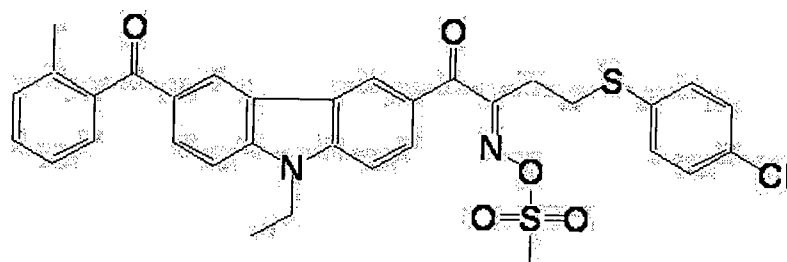
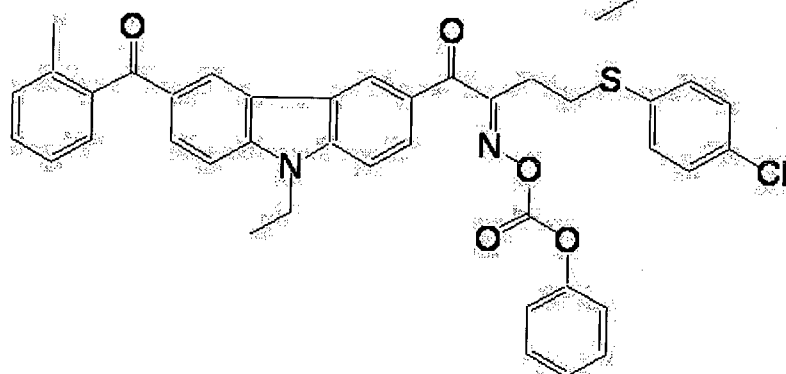
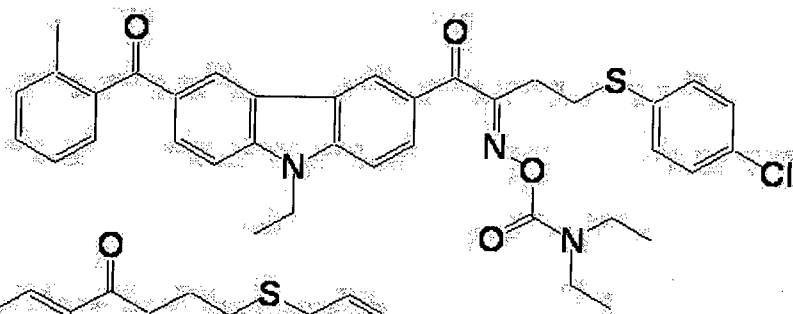
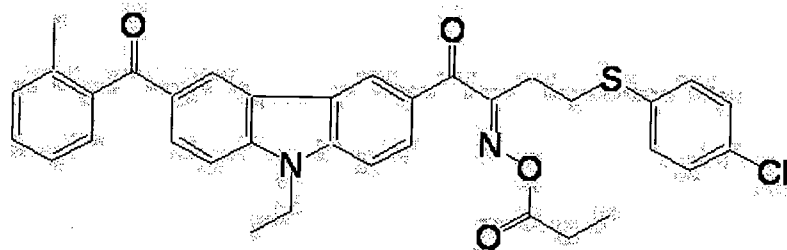
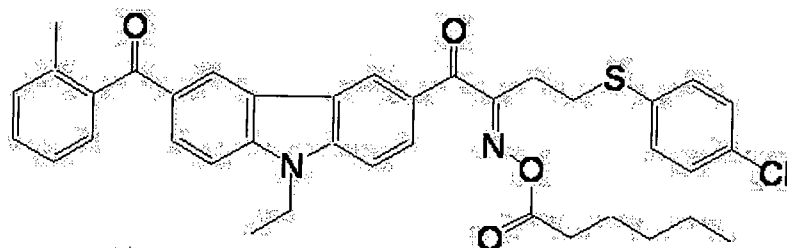
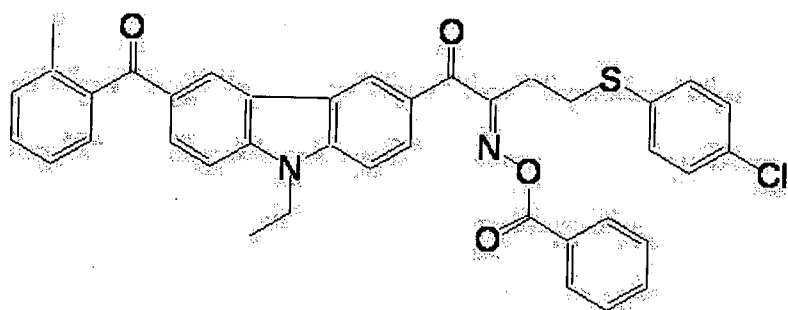


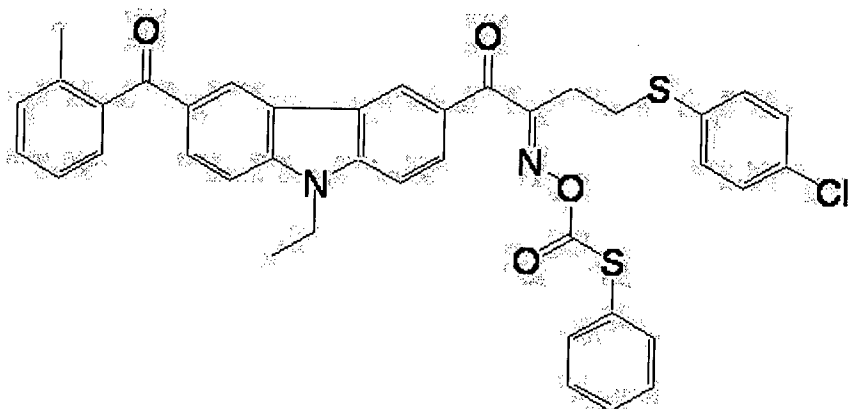
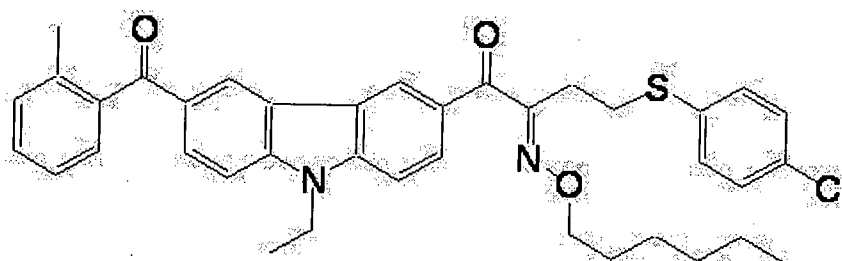
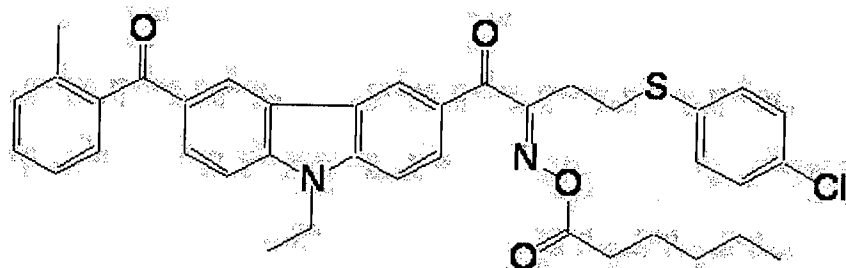
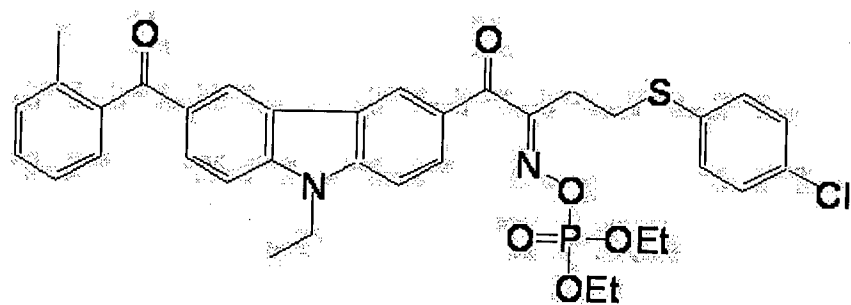
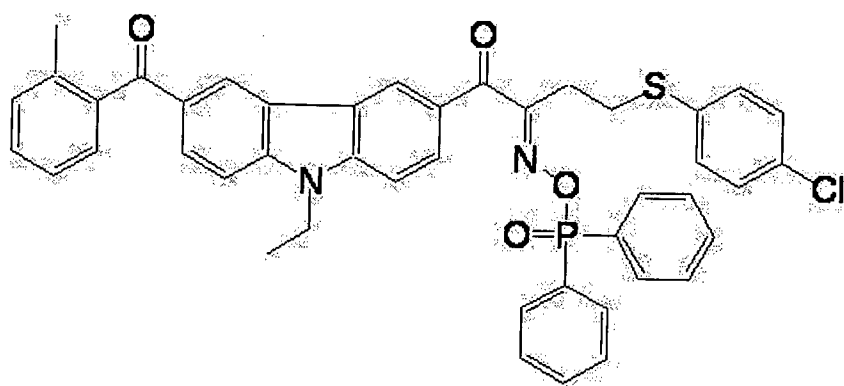
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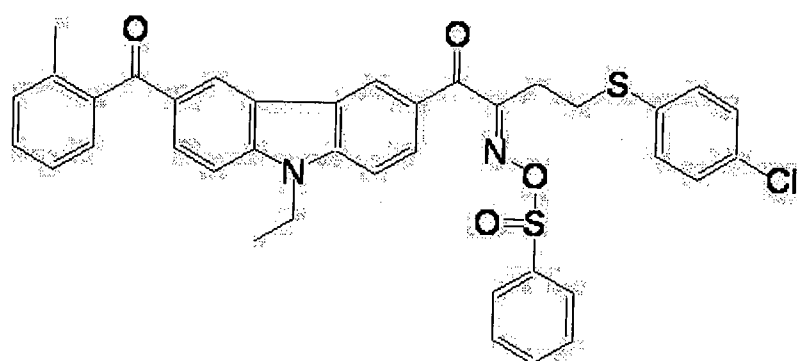
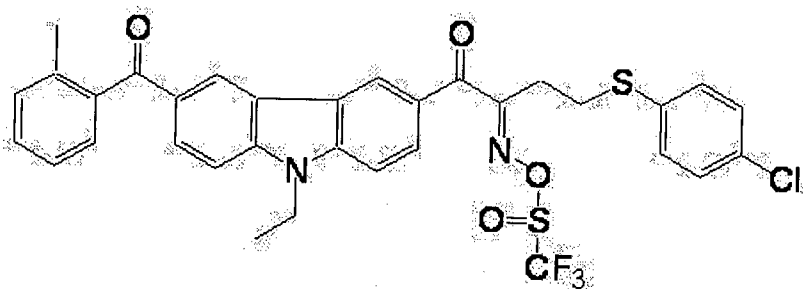
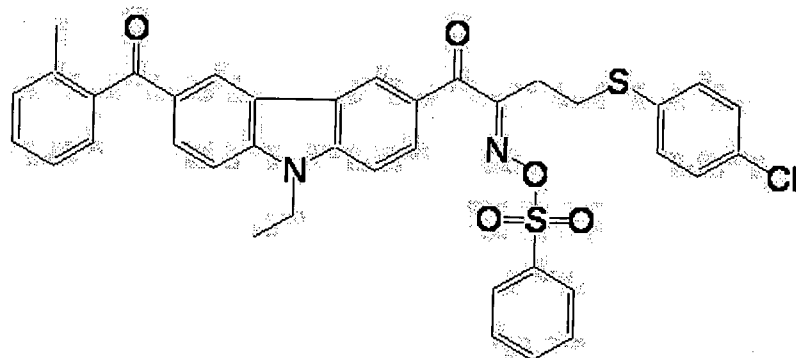
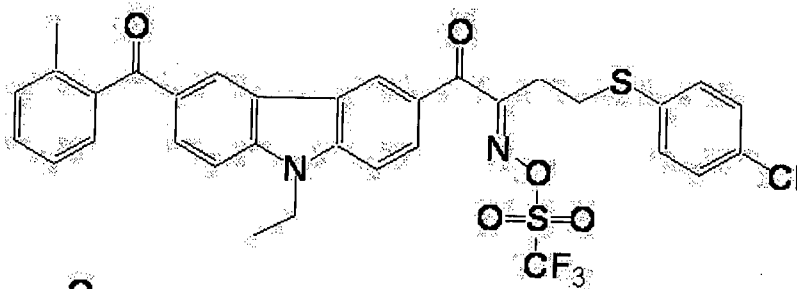
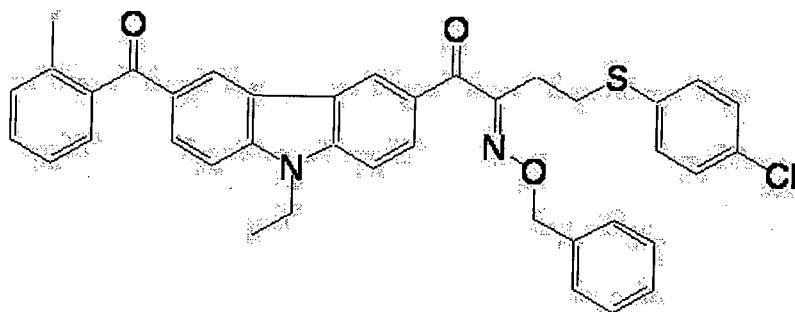


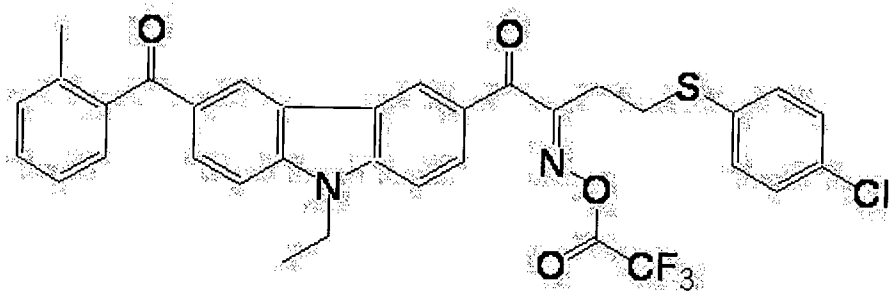
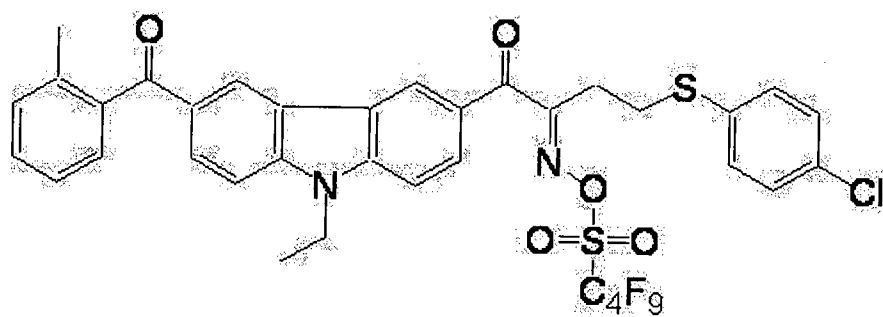
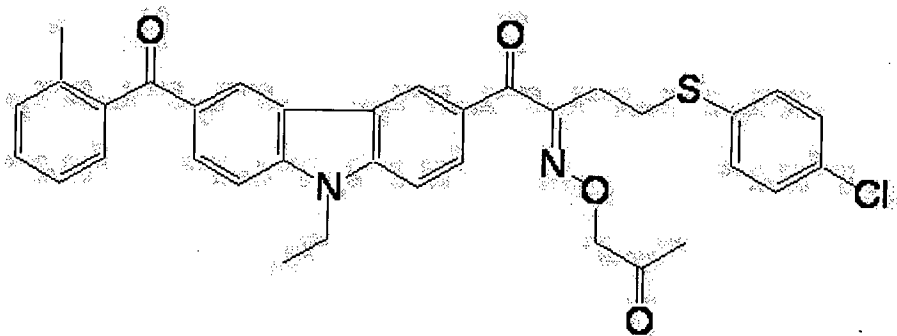
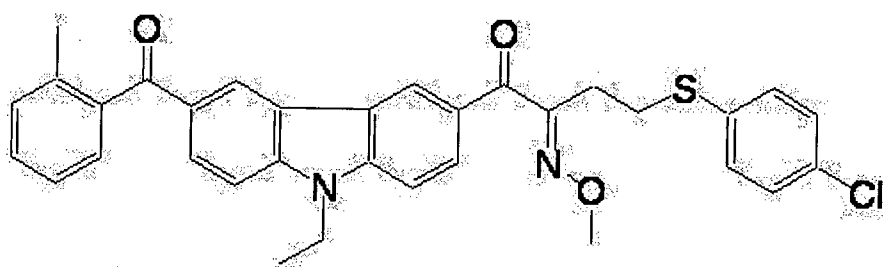
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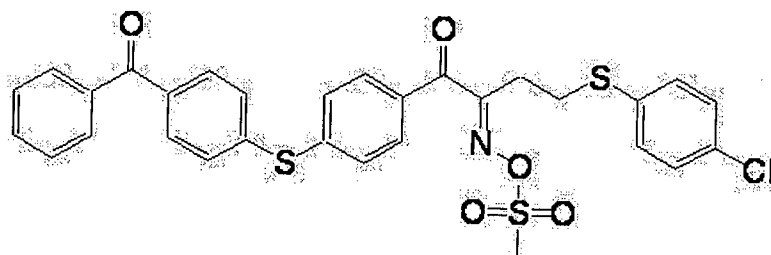
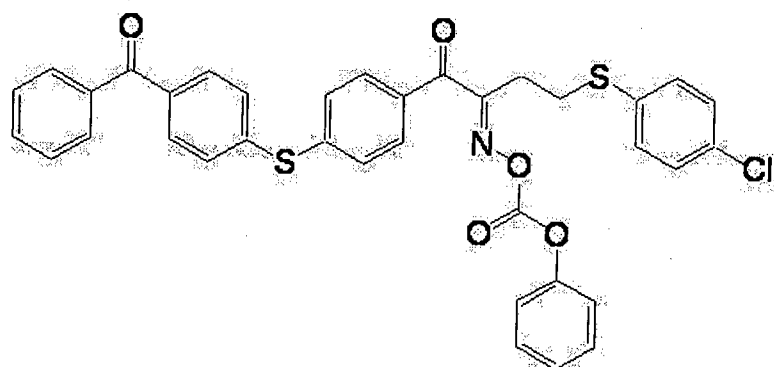
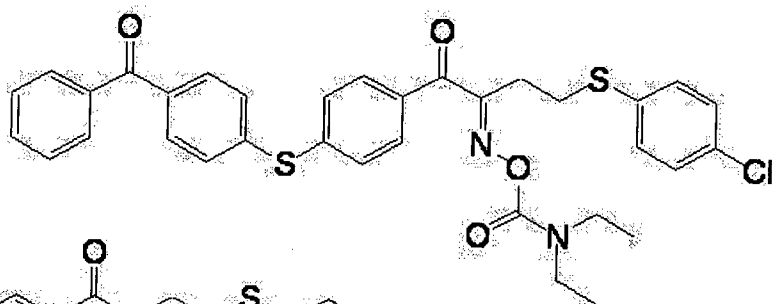
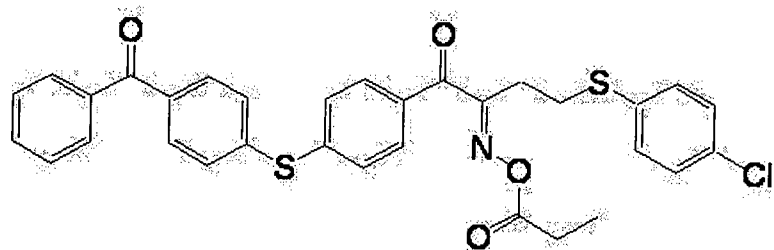
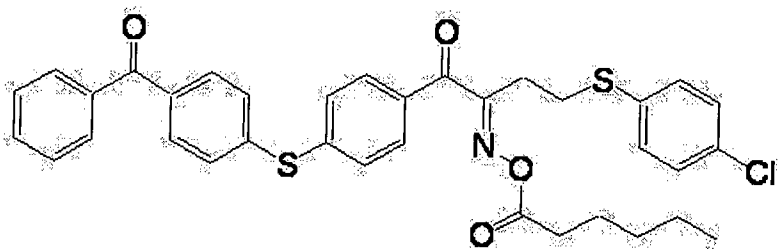
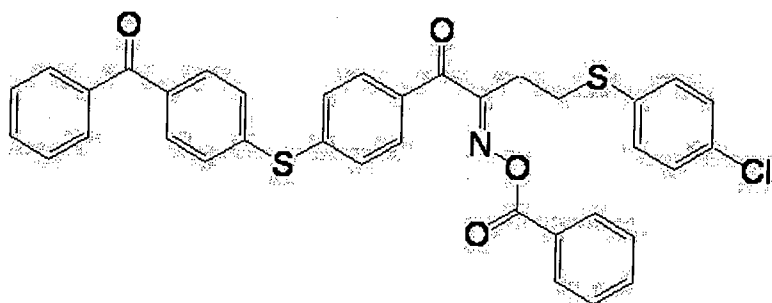


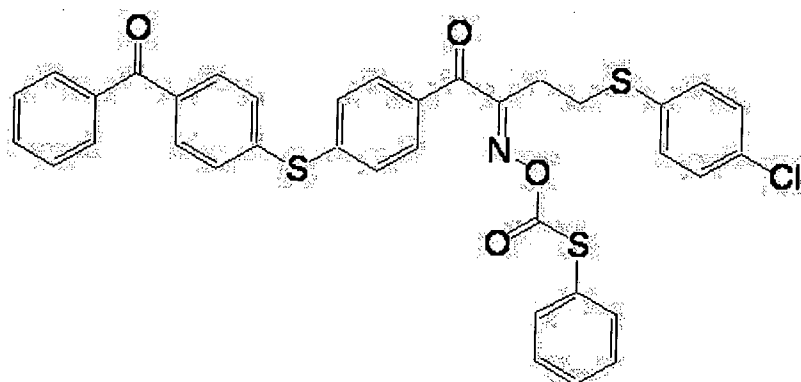
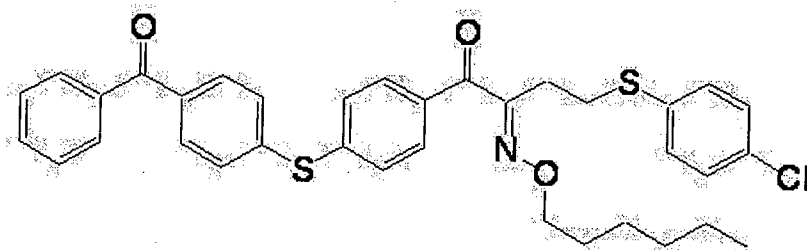
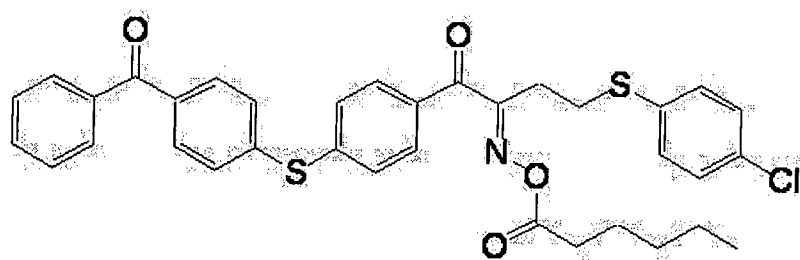
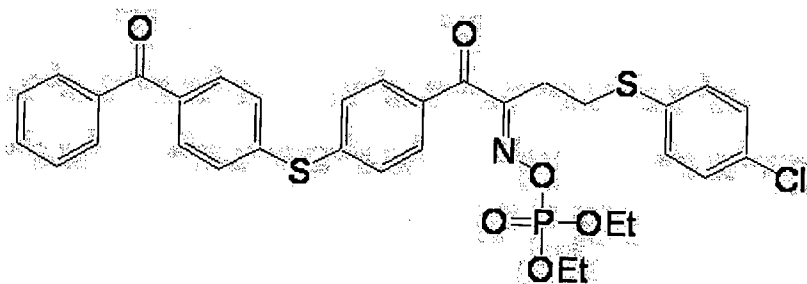
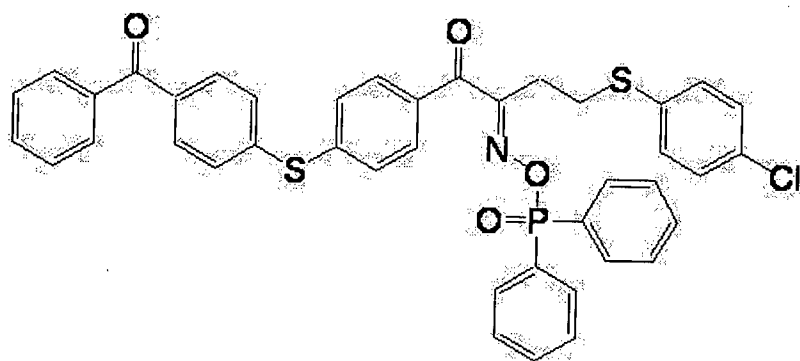


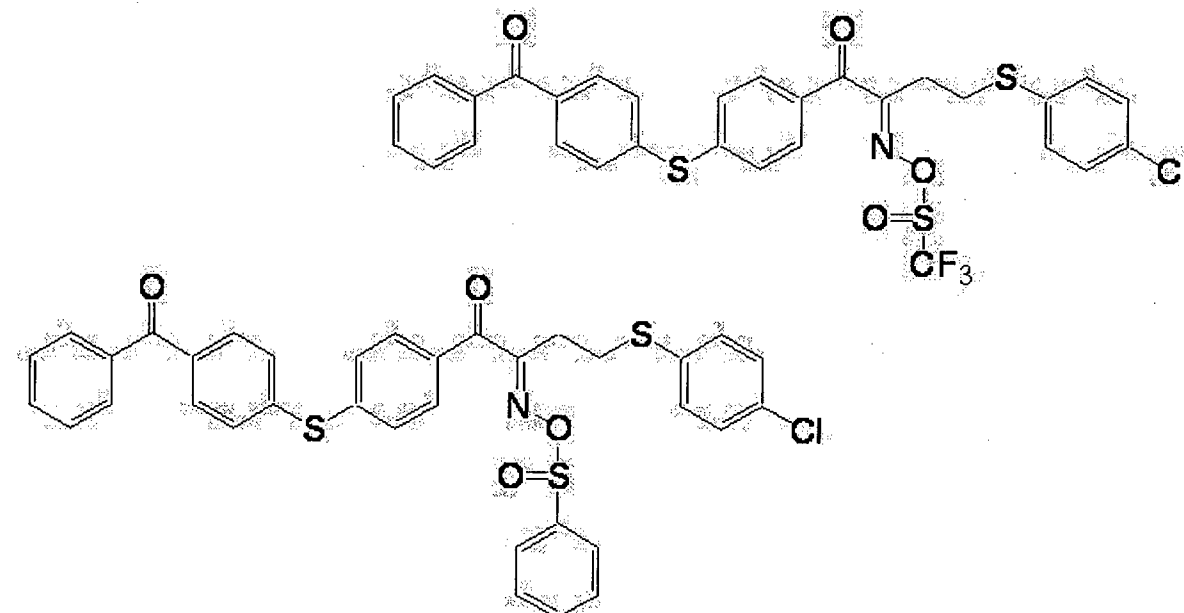
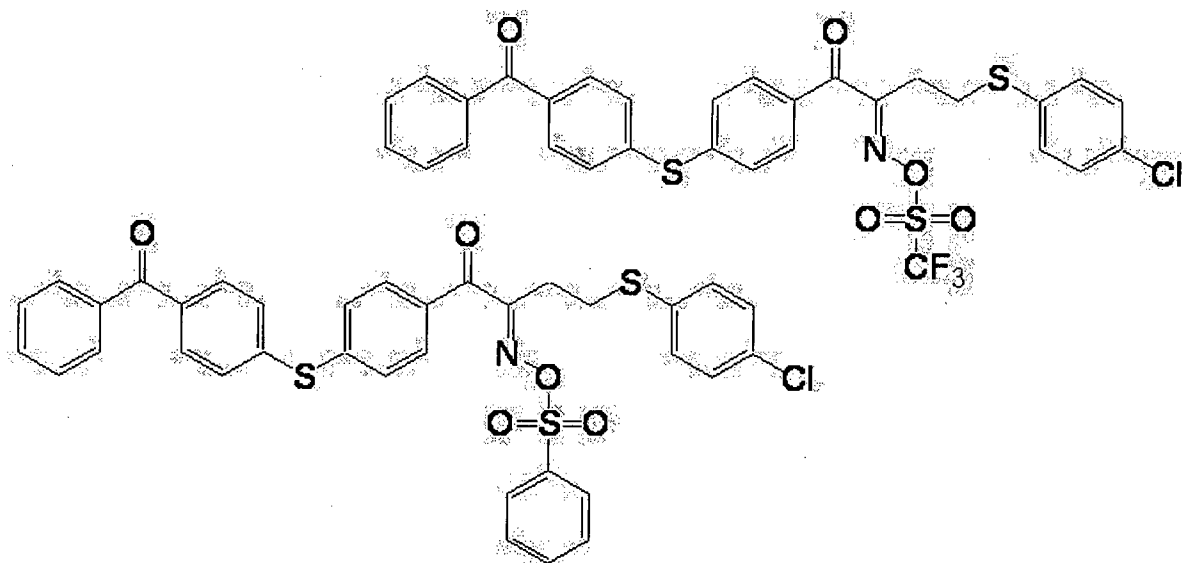
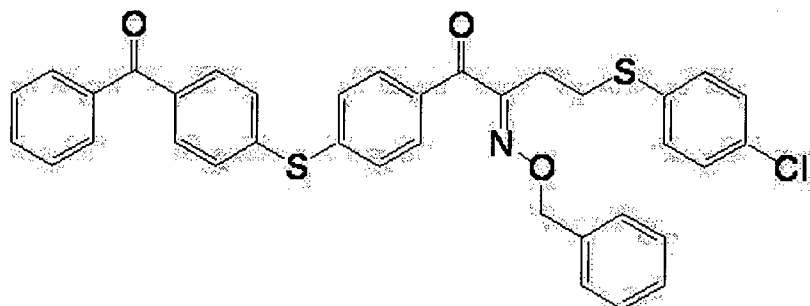


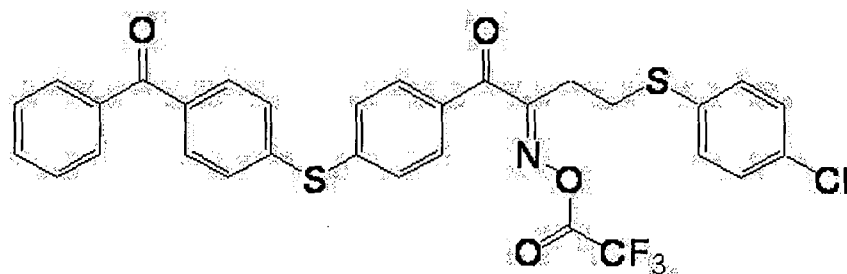
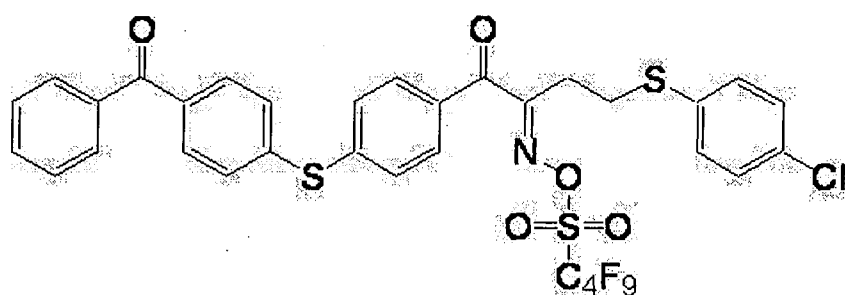
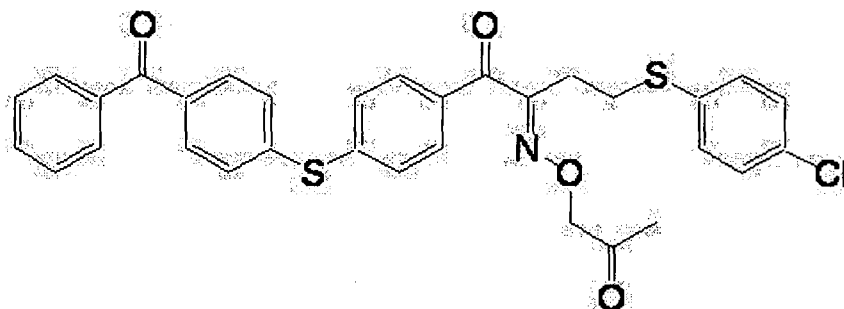
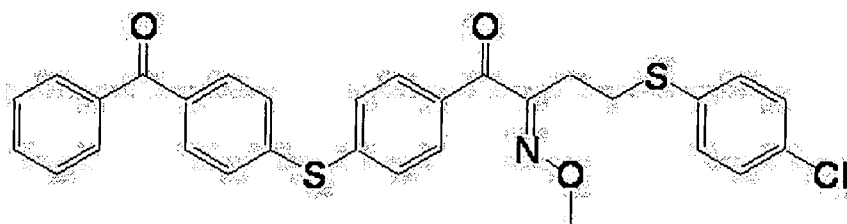












Oxime compounds have function as a thermal polymerization initiator that decomposes by heat and initiates and promotes the polymerization. In particular, the oxime compound represented by formula (a) is low in coloration at the time of post-heating and has excellent curability.

The oxime compound used in the present invention has preferably a maximum absorption wavelength in the wavelength region of from 350 nm to 500 nm and more preferably an absorption wavelength in the wavelength region of from 360 nm to 480 nm, and it is particularly preferred that the oxime compound has a high absorbance of 365 nm and 405 nm.

In the oxime compound, the molar absorption coefficient in 365 nm or 405 nm is

preferably from 1,000 to 300,000, more preferably from 2,000 to 300,000 and particularly preferably 5,000 to 200,000, from the viewpoint of sensitivity.

The molar absorption coefficient of the compound may be measured by using a known method, and specifically, it is preferred that the coefficient is measured, for example, by an ultraviolet and visible spectrophotometer (Carry-5 spectrophotometer, manufactured by Varian Inc.) at a concentration of 0.01 g/L using an ethyl acetate solvent.

As the oxime compound, commercially available products such as IRGACURE OXE01 and IRGACURE OXE02 (all manufactured by BASF Corporation), may be suitably used.

Examples of the onium salt compound include diazonium salts described in S. I. Schlesinger, *Photogr. Sci. Eng.*, 18, 387 (1974), and T. S. Bal et al., *Polymer*, 21, 423 (1980), ammonium salts described in U.S. Pat. No. 4,069,055, Japanese Patent Application Laid-Open No. H4-365049, and the like, phosphonium salts described in U.S. Pat. Nos. 4,069,055 and 4,069,056, iodonium salts described in European Patent No. 104,143, Japanese Patent Application Laid-Open Nos. H2-150848 and H2-296514, and the like.

The iodonium salt that may be suitably used in the present invention is a diaryl iodonium salt, and from the viewpoint of stability, it is preferred that the iodonium salt is substituted with two or more electron donating groups such as an alkyl group, an alkoxy group and an aryloxy group.

Examples of the sulfonium salt that is suitably used in the present invention include sulfonium salts described in European Patent Nos. 370,693, 390,214, 233,567, 297,443 and 297,442, U.S. Pat. Nos. 4,933,377, 4,760,013, 4,734,444 and 2,833,827, and German Patent Nos. 2,904,626, 3,604,580 and 3,604,581, and the sulfonium salts are preferably substituted with an electron-withdrawing group from the viewpoint of stability and sensitivity. The Hammett value of the electron-withdrawing group is preferably larger than zero. Preferred examples of the electron-withdrawing group include a halogen atom, a carboxylic acid group and the like.

Other preferred examples of the sulfonium salt include a sulfonium salt in which one of the substituent groups of a triaryl sulfonium salt has a coumarin structure or an anthraquinone structure, the sulfonium salt having absorption at 300 nm or more. Still other preferred examples of the sulfonium salt include a sulfonium salt, in which a triaryl sulfonium salt has an allyloxy group or an arylthio group in a substituent group, the sulfonium salt having absorption at 300 nm or more.

Examples of the onium salt include onium salts such as a selenonium salt described in J. V. Crivello et al., *Macromolecules*, 10(6), 1307 (1977) and J. V. Crivello et al., *J. Polymer Sci., Polymer Chem. Ed.*, 17, 1047 (1979), and an arsonium salt described in C. S. Wen et al., *Teh, Proc. Conf. Rad. Curing ASIA*, p. 478, Tokyo, October (1988).

Examples of the acyl phosphine (oxide) compound include IRGACURE 819, DAROCURE 4265, DAROCURE TPO, and the like, which are manufactured by BASF Corporation.

From the viewpoint of the curability, (E) the polymerization initiator used in the curable composition of the present invention is preferably a compound selected from the group consisting of a trihalomethyl triazine compound, a benzyl dimethyl ketal compound, an α -hydroxyketone compound, an α -aminoketone compound, an acyl phosphine compound, a phosphine oxide compound, a metallocene compound, an oxime compound, a triallylimidazole dimer, an onium compound, a benzothiazole compound, a benzophenone compound, an acetophenone compound and the derivatives thereof, a cyclopentadiene-benzene-iron complex and the salts thereof, a halomethyl oxadiazole compound and a 3-aryl-substituted coumarin compound.

A trihalomethyl triazine compound, an α -aminoketone compound, an acyl phosphine compound, a phosphine oxide compound, an oxime compound, a triallyl imidazole dimer, an onium compound, a benzophenone compound and an acetophenone compound are more preferred, and at least one compound selected from the group consisting of a trihalomethyl triazine compound, an α -aminoketone compound, an oxime compound, a triallyl imidazole dimer, and a benzophenone compound is most preferred.

In particular, when the curable composition of the present invention is formed on a color filter of a solid-state image sensing device to be manufactured into a microlens, in particular, the composition is low in coloration at the time of post-heating and also has excellent curability, and thus, it is most preferred that an oxime compound is used as (E) the polymerization initiator.

The content of (E) the polymerization initiator contained in the curable composition of the present invention is preferably from 0.1 mass% to 10 mass%, more preferably from 0.3 mass% to 8 mass%, and even more preferably from 0.5 mass% to 5 mass%, based on the total solid content of the curable composition. Within these ranges, good curability may be obtained.

The curable composition of the invention may further contain an arbitrary component

as described in detail below, if needed. Hereinafter, the arbitrary component which the curable composition may contain will be described.

[Sensitizer]

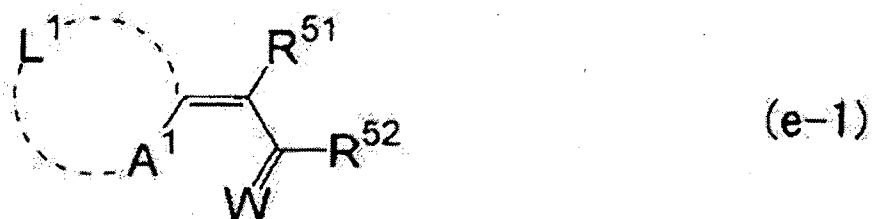
The curable composition of the present invention may contain a sensitizer for the purpose of improving radical generation efficiency of (E) the polymerization initiator, and shifting the sensitive wavelength to a longer wavelength.

The sensitizer that may be used in the present invention preferably sensitizes (E) the polymerization initiator by the electron transfer mechanism or the energy transfer mechanism.

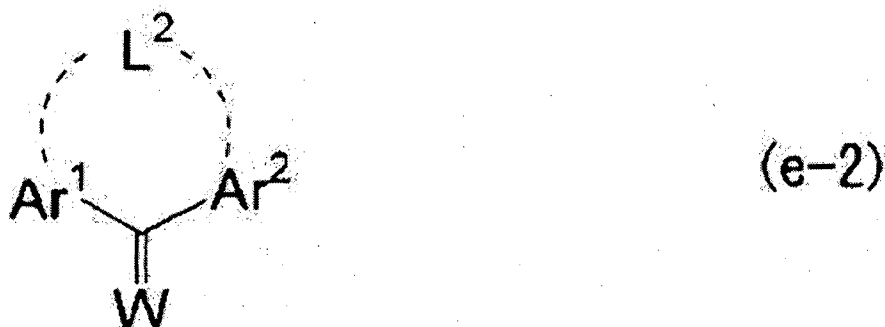
Examples of the sensitizer include sensitizers that belong to the compounds to be listed below and have an absorption wavelength in the wavelength region of from 300 nm to 450 nm.

That is, examples thereof include polynuclear aromatic groups (for example, phenanthrene, anthracene, pyrene, perylene, triphenylene and 9,10-dialkoxy anthracene), xanthenes (for example, fluorescein, eosin, erythrosine, Rhodamine B and rose bengal), thioxanthenes (isopropylthioxanthone, diethylthioxanthone and chlorothioxanthone), cyanines (for example, thiocarbocyanine and oxacarbocyanine), merocyanines (for example, merocyanine and carbomerocyanine), phthalocyanines, thiazines (for example, thionine, Methylene Blue and Toluidine Blue), acridines (for example, acridine orange, chloroflavin and acriflavine), anthraquinones (for example, anthraquinone), squaryliums (for example, squarylium), acridine orange, coumarins (for example, 7-diethylamino-4-methylcoumarin), ketocoumarin, phenothiazines, phenazines, styryl benzenes, azo compounds, diphenylmethane, triphenylmethane, distyryl benzenes, carbazoles, porphyrin, spiro compounds, quinacridone, indigo, styryl, pyrylium compounds, pyrromethene compounds, pyrazolotriazole compounds, benzothiazole compounds, barbituric acid derivatives, thiobarbituric acid derivatives, aromatic ketone compounds such as acetophenone, benzophenone, thioxanthone and Michler's ketone, and heterocyclic compounds such as N-aryloxazolidinone.

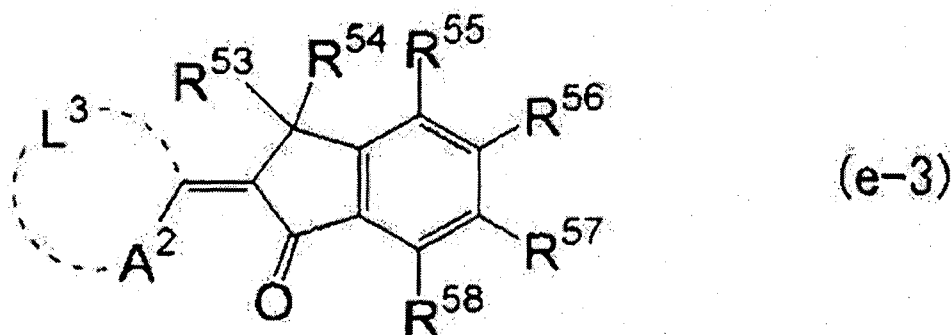
More preferred examples of the sensitizer that may be used in the present invention include compounds represented by the following general Formulas (e-1) to (e-4).



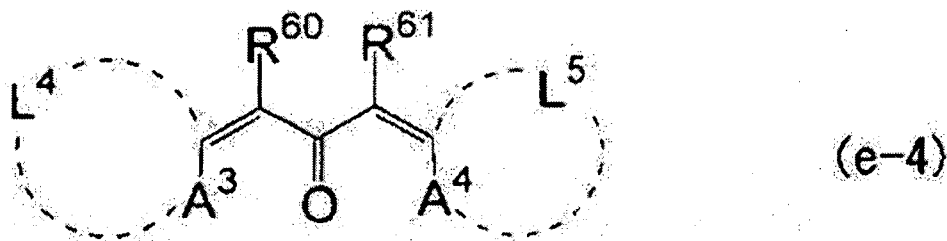
In formula (e-1), A^1 represents a sulfur atom or NR^{50} , R^{50} represents an alkyl group or an aryl group, L^1 represents a non-metal atomic group that forms a basic nucleus of the dye, together with A^1 and carbon atoms which are adjacent to L^1 , each of R^{51} and R^{52} independently represents a hydrogen atom or a monovalent non-metal atomic group, and R^{51} and R^{52} may be bonded to each other to form an acidic nucleus of the dye. W represents an oxygen atom or a sulfur atom.



In formula (e-2), each of Ar^1 and Ar^2 independently represents an aryl group, and Ar^1 and Ar^2 are linked with each other via the bond $-L^2-$ therebetween. Here, $-L^2-$ represents $-O-$ or $-S-$. W is the same as what is described in formula (e-1).



In formula (e-3), A^2 represents a sulfur atom or NR^{59} , L^3 represents a non-metal atomic group that forms a basic nucleus of the dye together with A^2 and carbon atoms, which are adjacent to L^3 , each of R^{53} , R^{54} , R^{55} , R^{56} , R^{57} and R^{58} independently represents a monovalent non-metal atomic group, and R^{59} represents an alkyl group or an aryl group.



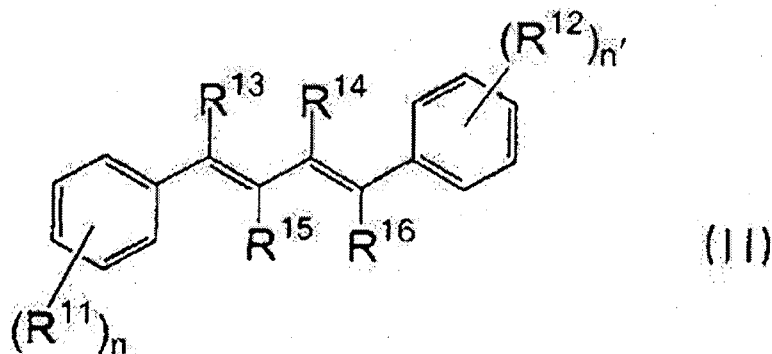
In formula (e-4), each of A^3 and A^4 independently represents $-S-$ or $-NR^{62}$, R^{62} represents a substituted or unsubstituted alkyl group, or a substituted or unsubstituted aryl group, L^4 represents a non-metal atomic group that forms a basic nucleus of the dye together with A^3 and carbon atoms, which are adjacent to L^4 , L^5 represents a non-metal atomic group that forms a basic nucleus of the dye together with A^4 and carbon atoms, which are adjacent to L^5 , and each of R^{60} and R^{61} independently represents a monovalent non-metal atomic group, or may be bonded to each other to form an aliphatic or aromatic ring.

The content of the sensitizer in the curable composition is preferably from 0.1 mass% to 20 mass% and more preferably from 0.5 mass% to 15 mass%, in terms of solid content from the viewpoint of light absorption efficiency to the deep portion and the decomposition efficiency of an initiator.

The sensitizers may be either alone or in combination of two or more thereof.

Examples of the preferable sensitizer that may be contained in the curable composition include at least one selected from the compound represented by the following general formula (II) and the compound represented by the general formula (III), in addition to the sensitizers.

The sensitizers may be either alone or in combination of two or more thereof.



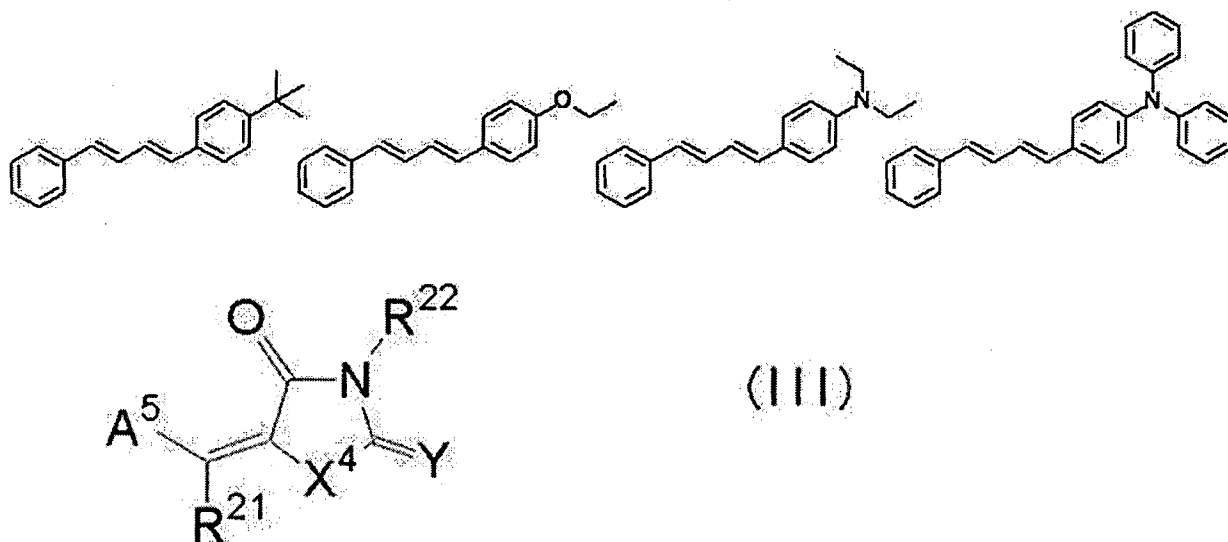
In formula (II), each of R^{11} and R^{12} independently represents a monovalent substituent group, and each of R^{13} , R^{14} , R^{15} and R^{16} independently represents a hydrogen atom or a monovalent substituent group. n represents an integer of from 0 to 5, n' represents an integer

of from 0 to 5, but there is no case where both n and n' are 0 at the same time. When n is two or more, each of a plurality of R^{11} 's may be the same as or different from every other R^{11} . When n' is two or more, each of a plurality of R^{12} 's may be the same as or different from every other R^{12} . Meanwhile, the formula (II) is not limited to any one of the isomers thereof by means of the double bonds.

The molar absorption coefficient ϵ of the compound represented by the general formula (II) is preferably $500 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ or more at a wavelength of 365 nm, more preferably $3,000 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ or more at a wavelength of 365 nm and most preferably $20,000 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ or more at a wavelength of 365 nm. It is preferred that the value of the molar absorption coefficient ϵ at each wavelength is within the above-described range, from the viewpoint of the light absorption efficiency because the effect of increasing the sensitivity is high.

Preferred specific examples of the compounds represented by the general formula (II) are illustrated below, but the present invention is not limited thereto.

Meanwhile, in the present specification, chemical formulas may be described by simplified structural formulas, and solid lines represent hydrocarbon groups, unless elements or substituent groups are otherwise specified.

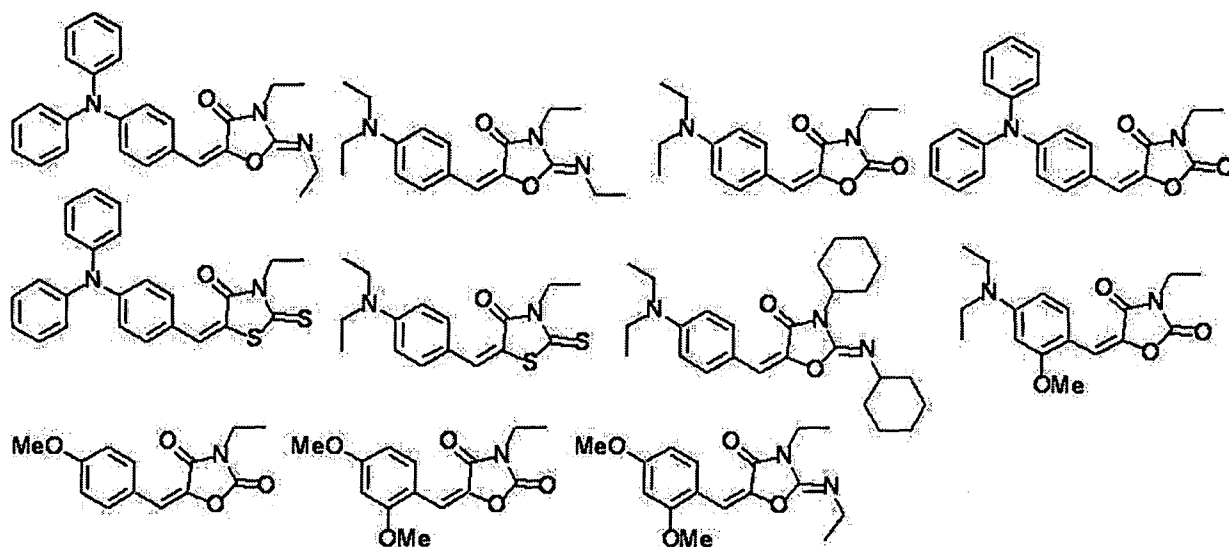


In the general formula (III), A^5 represents an aromatic ring or heterocyclic ring which may have a substituent group, X^4 represents an oxygen atom, a sulfur atom, or $-\text{N}(\text{R}^{23})-$, and Y represents an oxygen atom, a sulfur atom, or $-\text{N}(\text{R}^{23})-$. Each of R^{21} , R^{22} and R^{23} independently represents a hydrogen atom or a monovalent non-metal atomic group, and each of A^5 , R^{21} , R^{22} and R^{23} may be bonded to one another to form an aliphatic or aromatic ring.

In the general formula (III), each of R^{21} , R^{22} and R^{23} independently represents a hydrogen atom or a monovalent non-metal atomic group. When each of R^{21} , R^{22} and R^{23} represents a monovalent non-metal atomic group, each of R^{21} , R^{22} and R^{23} is preferably a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted aromatic heterocyclic residue, a substituted or unsubstituted alkoxy group, a substituted or unsubstituted alkylthio group, a hydroxyl group, or a halogen atom.

In a compound represented by the general formula (III), Y is preferably an oxygen atom or $-N(R^{23})-$, from the viewpoint of improving the decomposition efficiency of the photopolymerization initiator. R^{23} represents a hydrogen atom or a monovalent non-metal atomic group. Y is most preferably $-N(R^{23})-$.

Hereinafter, preferred specific examples of the compounds represented by the general formula (III) will be shown, but the present invention is not limited thereto. The isomers by means of the double bond that connects the acidic nucleus and the basic nucleus are not specified, and the present invention is not limited to any one of the isomers.



[Co-Sensitizer]

It is preferred that the curable composition of the present invention also contains a co-sensitizer.

In the present invention, the co-sensitizer has the function of further increasing the sensitivity of (E) the polymerization initiator or a sensitizer to the active radiation, suppressing the polymerization inhibition of (D) the polymerizable compound due to oxygen, and the like.

Examples of such co-sensitizers include amines, for example, compounds described in "Journal of Polymer Society", Vol. 10, p. 3173 (1972) written by M. R. Sander et al., Japanese Patent Publication No. S44-20189, Japanese Patent Application Laid-Open Nos. S51-82102, S52-134692, S59-138205, S60-84305, S62-18537, and S64-33104, and Research Disclosure No. 33825. Specific examples thereof include triethanol amine, ethyl p-dimethylaminobenzoate, p-formyldimethylaniline, p-methylthiodimethylaniline and the like.

Other examples of the co-sensitizers include thiols and sulfides, for example, thiol compounds described in Japanese Patent Application Laid-Open No. S53-702, Japanese Patent Publication No. S55-500806, and Japanese Patent Application Laid-Open No. H5-142772, disulfide compounds described in Japanese Patent Application Laid-Open No. S56-75643 and the like. Specific examples thereof include 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-mercaptobenzimidazole, 2-mercapto-4(3H)-quinazoline, β -mercaptanaphthalene and the like.

Still other examples of the co-sensitizers include amino acid compounds (for example, N-phenylglycine and the like), organic metal compounds described in Japanese Patent Publication No. S48-42965 (for example, tributyl tin acetate and the like), a hydrogen donor described in Japanese Patent Publication No. S55-34414, sulfur compounds (for example, trithiane and the like) described in Japanese Patent Application Laid-Open No. H6-308727, and the like.

The content of the co-sensitizers is preferably in the range of from 0.1 mass% to 30 mass%, more preferably in the range of from 1 mass% to 25 mass% and even more preferably in the range of from 1.5 mass% to 20 mass%, based on the total solid content mass of the curable composition from the viewpoint of increasing the curing rate by means of the balance of the polymerization growth rate and the chain transfer.

[Polymerization Inhibitor]

In the present invention, in order to prevent unnecessary polymerization of a compound having a polymerizable ethylenically unsaturated double bond during the preparation or the storage of the curable composition, it is preferable to add a polymerization inhibitor.

Examples of the polymerization inhibitor that may be used in the present invention include a phenolic hydroxyl group-containing compound, N-oxide compounds, piperidine-1-oxyl free radical compounds, pyrrolidine-1-oxyl free radical compounds, N-nitrosophenyl hydroxylamines, diazonium compounds, cationic dyes, sulfide

group-containing compounds, nitro group-containing compounds, transition metal compounds such as FeCl_3 or CuCl_2 .

More preferred aspects are as follows.

The phenolic hydroxyl group-containing compound is preferably a compound selected from the group consisting of hydroquinone, p-methoxyphenol, di-t-butyl-p-cresol, pyrogallol, t-butyl catechol, benzoquinone, 4,4-thiobis(3-methyl-6-t-butylphenol), 2,2'-methylenebis(4-methyl-6-t-butylphenol), phenol resins and cresol resins.

The N-oxide compounds are preferably a compound selected from the group consisting of 5,5-dimethyl-1-pyrroline N-oxide, 4-methylmorpholine N-oxide, pyridine N-oxide, 4-nitropyridine N-oxide, 3-hydroxypyridine N-oxide, picolinic acid N-oxide, nicotinic acid N-oxide and isonicotinic acid N-oxide.

The piperidine-1-oxyl free radical compounds are preferably a compound selected from the group consisting of piperidine-1-oxyl free radical, 2,2,6,6-tetramethyl piperidine-1-oxyl free radical, 4-oxo-2,2,6,6-tetramethyl piperidine-1-oxyl free radical, 4-hydroxy-2,2,6,6-tetramethyl piperidine-1-oxyl free radical, 4-acetamide-2,2,6,6-tetramethyl piperidine-1-oxyl free radical, 4-maleimide-2,2,6,6-tetramethyl piperidine-1-oxyl free radical and 4-phosphonoxy-2,2,6,6-tetramethyl piperidine-1-oxyl free radical.

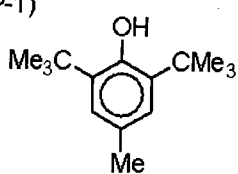
The pyrrolidine-1-oxyl free radical compounds are preferably 3-carboxyproxyl free radical (3-carboxy-2,2,5,5-tetramethylpyrrolidine-1-oxyl free radical).

The N-nitrosophenylhydroxylamines are preferably a compound selected from the group consisting of N-nitrosophenylhydroxylamine cerium (I) salt and N-nitrosophenylhydroxylamine aluminum salt.

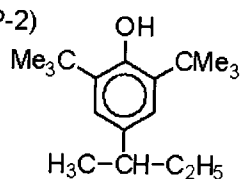
The diazonium compounds are preferably a compound selected from the group consisting of 4-diazophenyldimethylamine hydrogensulfate, 4-diazodiphenylamine tetrafluoroborate and 3-methoxy-4-diazodiphenylamine hexafluorophosphate.

Suitable polymerization inhibitors that may be used in the present invention are illustrated below, but the present invention is not limited thereto. Meanwhile, phenol polymerization inhibitors include the following exemplary compounds (P-1) to (P-24).

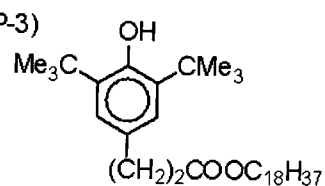
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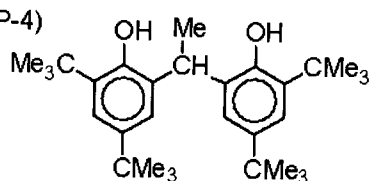
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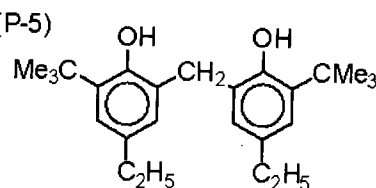
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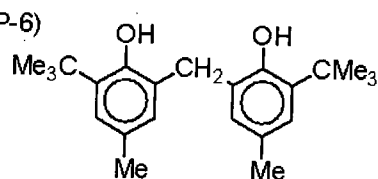
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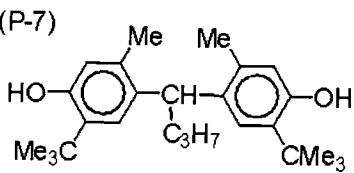
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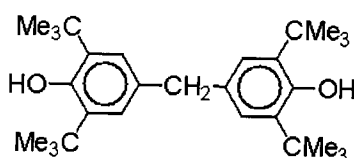
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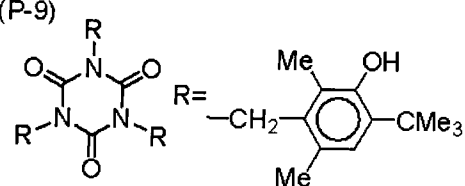
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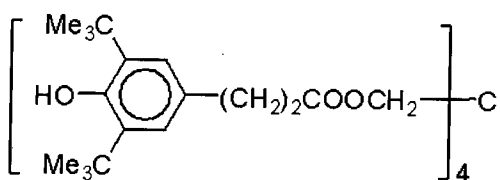
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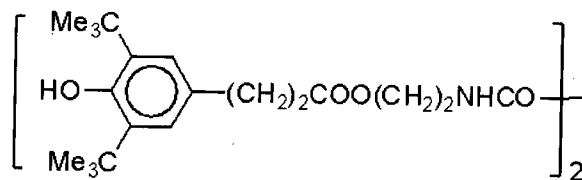
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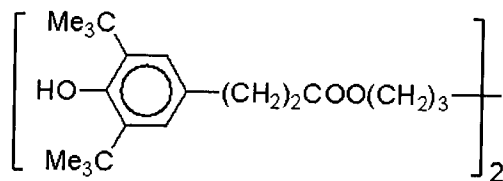
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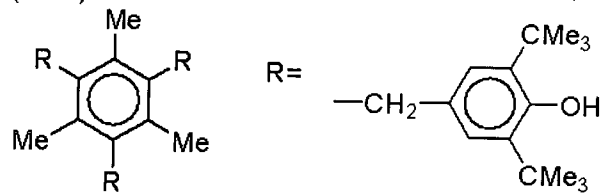
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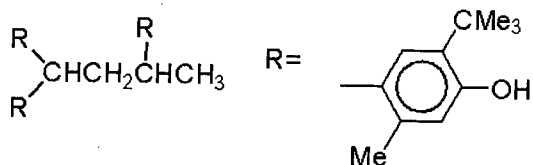
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(P-13)

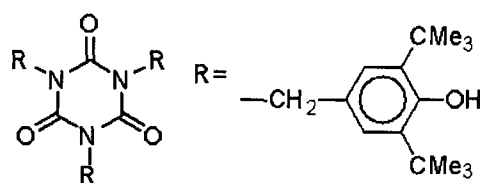


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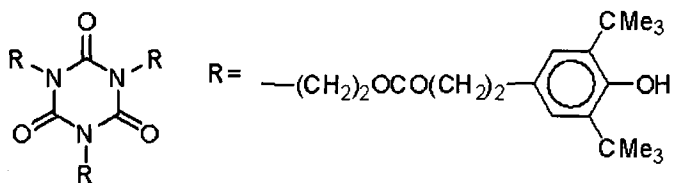


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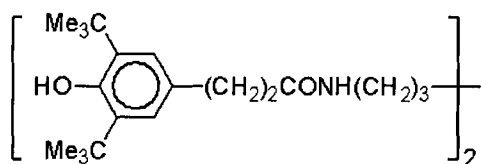
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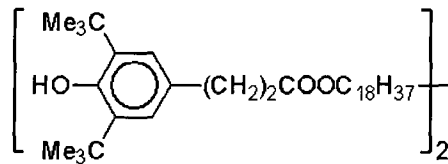
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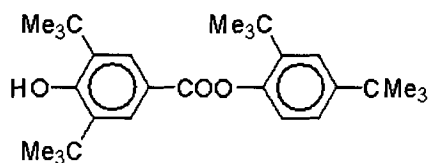
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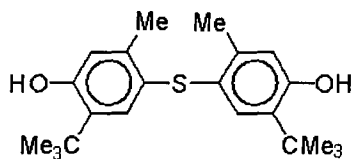
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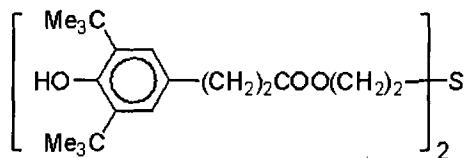
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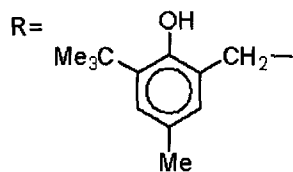
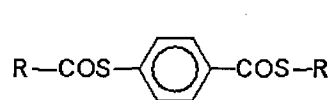
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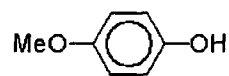
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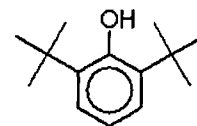
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(P-23)

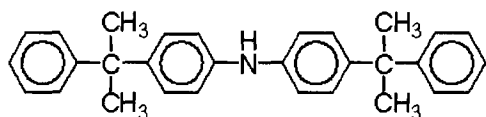


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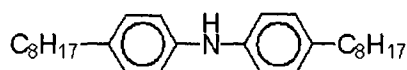


Amine polymerization inhibitors include the following exemplary compounds (N-1) to (N-7).

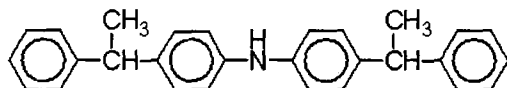
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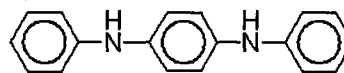
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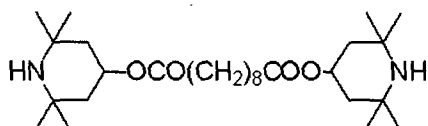
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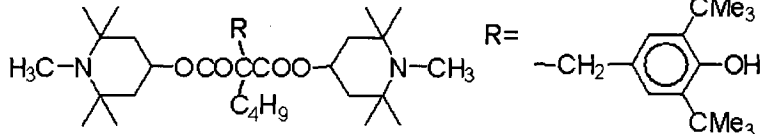
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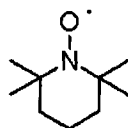
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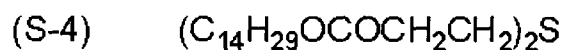
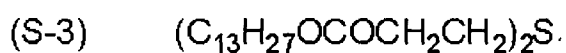
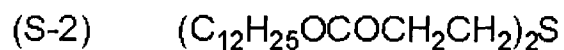
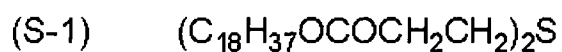
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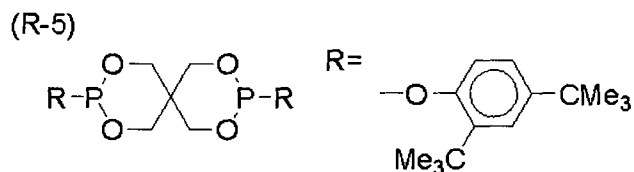
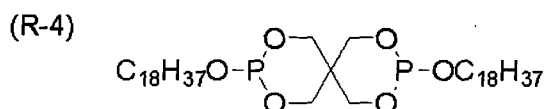
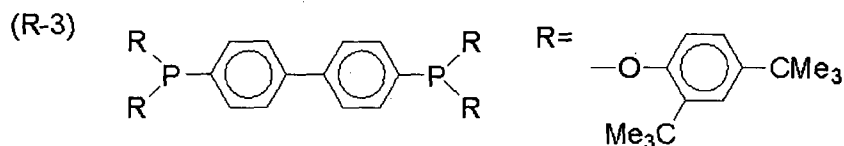
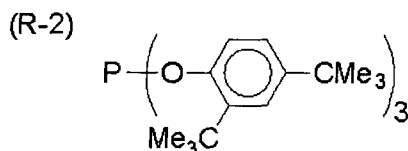
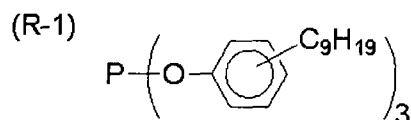
(N-7)



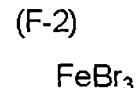
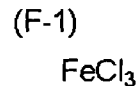
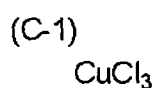
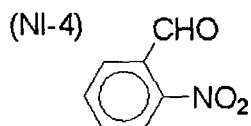
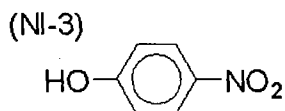
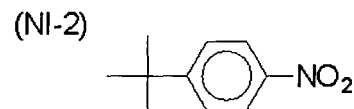
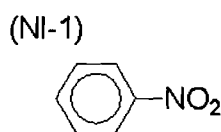
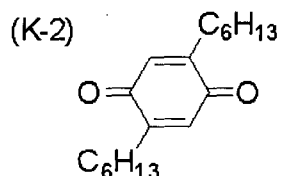
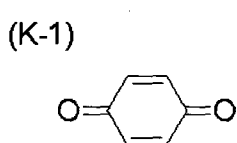
Sulfur-based polymerization inhibitors include the following exemplary compounds (S-1) to (S-5).



Phosphite-based polymerization inhibitors include the following exemplary compounds (R-1) to (R-5).



Each of the following compounds may also be used as a suitable polymerization inhibitor.



Among the above-described exemplary compounds, preferred examples thereof include a phenolic hydroxyl group-containing compound such as hydroquinone, p-methoxyphenol, di-t-butyl-p-cresol, pyrogallol, t-butyl catechol, benzoquinone, 4,4-thiobis(3-methyl-6-t-butylphenol) and 2,2'-methylene-bis(4-methyl-6-t-butylphenol), piperidine-1-oxyl free radical compounds, or a piperidine-1-oxyl free radical compound such as 2,2,6,6-tetramethylpiperidine-1-oxyl free radical, 4-oxo-2,2,6,6-tetramethyl piperidine-1-oxyl free radical, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl free radical, 4-acetamide-2,2,6,6-tetramethylpiperidine-1-oxyl free radical, 4-maleimide-2,2,6,6-tetramethylpiperidine-1-oxyl free radical and 4-phosphonoxy-2,2,6,6-tetramethylpiperidine-1-oxyl free radical, or an N-nitrosophenylhydroxylamine compound such as N-nitrosophenylhydroxylamine cerium (I)

salt and N-nitrosophenylhydroxylamine aluminum salt, more preferred examples include a piperidine-1-oxyl free radical compound such as 2,2,6,6-tetramethylpiperidine-1-oxyl free radical, 4-oxo-2,2,6,6-tetramethyl piperidine-1-oxyl free radical, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl free radical, 4-acetamide-2,2,6,6-tetramethylpiperidine-1-oxyl free radical, 4-maleimide-2,2,6,6-tetramethylpiperidine-1-oxyl free radical and 4-phosphonoxy-2,2,6,6-tetramethylpiperidine-1-oxyl free radical, or an N-nitrosophenylhydroxylamine compounds such as N-nitrosophenylhydroxylamine cerium (I) salt and N-nitrosophenylhydroxylamine aluminum salt, and even more preferred examples thereof include an N-nitrosophenylhydroxylamine compound such as N-nitrosophenylhydroxylamine cerium (I) salt and N-nitrosophenylhydroxylamine aluminum salt.

The amount of the polymerization inhibitor to be added is preferably from 0.01 part by mass to 10 parts by mass, more preferably from 0.01 part by mass to 8 parts by mass, and most preferably from 0.05 part by mass to 5 parts by mass, based on 100 parts by mass of (E) the polymerization initiator.

By setting the amount to be within the above-described ranges, the suppression of curing reaction in a non-image area, and the promotion of curing reaction in an image area may be sufficiently achieved, and thus, the image formability and the sensitivity become good.

[Binder Polymer]

It is preferred that the curable composition of the present invention further contains a binder polymer from the viewpoint of improving coating film properties, and the like.

As the binder polymer, it is preferred to use a linear organic polymer. As the linear organic polymer, any known polymer may be arbitrarily used. In order to enable water development or weak alkaline-water development, a linear organic polymer that is soluble or swellable in water or weak alkaline water is preferably selected. The linear organic polymer is selectively used in accordance with the use not only as a film-forming agent but as water, weak alkaline water or an organic solvent developer. For example, when a water-soluble organic polymer is used, water development becomes possible. Examples of such linear organic polymers include a radical polymer having a carboxyl acid group in the side chain thereof, for example, polymers described in Japanese Patent Application Laid-Open No. S59-44615, Japanese Patent Publication Nos. S54-34327, S58-12577 and S54-25957, Japanese

Patent Application Laid-Open Nos. S54-92723, S59-53836 and S59-71048, that is, a resin formed by homopolymerization or copolymerization of a monomer having a carboxyl group, a resin formed by hydrolyzing, half-esterifying or half-amidizing an acid anhydride unit formed by homopolymerization or copolymerization of a monomer having an acid anhydride, an epoxy acrylate formed by modifying an epoxy resin with an unsaturated monocarboxylic acid and an acid anhydride, and the like. Examples of the monomer having a carboxyl group include acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, 4-carboxyl styrene and the like, and examples of the monomer having an acid anhydride include anhydrous maleic acid and the like.

An acidic cellulose derivative having a carboxylic acid group similarly in the side chain thereof is included. A polymer formed by adding a cyclic acid anhydride to a polymer having a hydroxyl group and the like are also useful.

In the present invention, when a copolymer is used as the binder polymer, monomers other than the monomers as described above may be used as a compound to be copolymerized. Examples of other monomers include the compounds described in the following (1) to (12).

(1) acrylic acid esters and methacrylic acid esters having an aliphatic hydroxyl group, such as 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 3-hydroxypropyl acrylate, 4-hydroxybutyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl methacrylate and 4-hydroxybutyl methacrylate.

(2) alkyl acrylate such as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, isobutyl acrylate, amyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, octyl acrylate, benzyl acrylate, 2-chloroethyl acrylate, glycidyl acrylate, 3,4-epoxycyclohexyl methylacrylate, vinyl acrylate, 2-phenylvinyl acrylate, 1-propenyl acrylate, allyl acrylate, 2-allyloxyethyl acrylate and propargyl acrylate.

(3) alkyl methacrylate such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, isobutyl methacrylate, amyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, 2-chloroethyl methacrylate, glycidyl methacrylate, 3,4-epoxycyclohexyl methylmethacrylate, vinyl methacrylate, 2-phenylvinyl methacrylate, 1-propenyl methacrylate, allyl methacrylate, 2-allyloxyethyl methacrylate and propargyl methacrylate.

(4) acrylamides or methacrylamides, such as acrylamide, methacrylamide, N-methylol acrylamide, N-ethyl acrylamide, N-hexyl methacrylamide, N-cyclohexyl acrylamide, N-hydroxyethyl acrylamide, N-phenyl acrylamide, N-nitrophenyl acrylamide,

N-ethyl-N-phenyl acrylamide, vinyl acrylamide, vinyl methacrylamide, N,N-diallyl acrylamide, N,N-diallyl methacrylamide, allylacrylamide and allylmethacryl amide.

(5) vinyl ethers such as ethyl vinyl ether, 2-chloroethyl vinyl ether, hydroxyethyl vinyl ether, propyl vinyl ether, butyl vinyl ether, octyl vinyl ether and phenyl vinyl ether.

(6) vinyl esters such as vinyl acetate, vinyl chloroacetate, vinyl butyrate and vinyl benzoate.

(7) styrenes such as styrene, α -methylstyrene, methylstyrene, chloromethylstyrene, p-acetoxystyrene, and the like.

(8) vinyl ketones such as methyl vinyl ketone, ethyl vinyl ketone, propyl vinyl ketone and phenyl vinyl ketone.

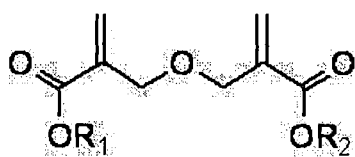
(9) olefins such as ethylene, propylene, isobutylene, butadiene and isoprene.

(10) N-vinyl pyrrolidone, acrylonitrile, methacrylonitrile and the like.

(11) unsaturated imide such as maleimide, N-acryloyl acrylamide, N-acetyl methacrylamide, N-propionyl methacrylamide and N-(p-chlorobenzoyl)methacrylamide.

(12) a methacrylic acid monomer in which a heteroatom is bonded to the α -position thereof, for example, compounds described in Japanese Patent Application Laid-Open Nos. 2002-309057 and No. 2003-311569, and the like, may be included.

In the binder polymer, it is also preferred to include a repeating unit formed by polymerizing a monomer component essentially including a compound represented by the following general formula (ED) (hereinafter, referred to as "ether dimer" in some cases).



(ED)

(In Formula (ED), each of R_1 and R_2 independently represents a hydrogen atom or a hydrocarbon group having from 1 to 25 carbon atoms, which may have a substituent group)

Accordingly, the curable resin composition of the present invention may form a cured coating film which has very excellent heat resistance as well as very excellent transparency. In the general formula (ED) representing the ether dimer, the hydrocarbon group having from 1 to 25 carbon atoms, which may have a substituent group represented by R_1 and R_2 is not particularly limited, but examples thereof include a straight-chained or branched alkyl group,

such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, t-amyl, stearyl, lauryl and 2-ethylhexyl; an aryl group such as phenyl; a cycloaliphatic group such as cyclohexyl, t-butyl cyclohexyl, dicyclopentadienyl, tricyclodecanyl, isobornyl, adamantyl and 2-methyl-2-adamantyl; an alkoxy-substituted alkyl group such as 1-methoxyethyl, 1-ethoxyethyl, and the like; an aryl group-substituted alkyl group such as benzyl; and the like. Among them, in particular, a primary or secondary carbon substituent group, such as methyl, ethyl, cyclohexyl and benzyl, which is not readily desorbed by acid or heat, is preferred from the viewpoint of heat resistance.

Specific examples of the ether dimer include dimethyl-2,2'-[oxybis(methylene)]bis-2-propenoate, diethyl-2,2'-[oxybis(methylene)]bis-2-propenoate, di(n-propyl)-2,2'-[oxybis(methylene)]bis-2-propenoate, di(isopropyl)-2,2'-[oxybis(methylene)]bis-2-propenoate, di(n-butyl)-2,2'-[oxybis(methylene)]bis-2-propenoate, di(isobutyl)-2,2'-[oxybis(methylene)]bis-2-propenoate, di(t-butyl)-2,2'-[oxybis(methylene)]bis-2-propenoate, di(t-amyl)-2,2'-[oxybis(methylene)]bis-2-propenoate, di(stearyl)-2,2'-[oxybis(methylene)]bis-2-propenoate, di(lauryl)-2,2'-[oxybis(methylene)]bis-2-propenoate, di(2-ethylhexyl)-2,2'-[oxybis(methylene)]bis-2-propenoate, di(1-methoxyethyl)-2,2'-[oxybis(methylene)]bis-2-propenoate, di(1-ethoxyethyl)-2,2'-[oxybis(methylene)]bis-2-propenoate, dibenzyl-2,2'-[oxybis(methylene)]bis-2-propenoate, biphenyl-2,2'-[oxybis(methylene)]bis-2-propenoate, dicyclohexyl-2,2'-[oxybis(methylene)]bis-2-propenoate, di(t-butylcyclohexyl)-2,2'-[oxybis(methylene)]bis-2-propenoate, di(dicyclopentadienyl)-2,2'-[oxybis(methylene)]bis-2-propenoate, di(tricyclodecanyl)-2,2'-[oxybis(methylene)]bis-2-propenoate, di(isobornyl)-2,2'-[oxybis(methylene)]bis-2-propenoate, diadamantyl-2,2'-[oxybis(methylene)]bis-2-propenoate, di(2-methyl-2-adamantyl)-2,2'-[oxybis(methylene)]bis-2-propenoate, and the like. Among them, in particular, dimethyl-2,2'-[oxybis(methylene)]bis-2-propenoate, diethyl-2,2'-[oxybis(methylene)]bis-2-propenoate,

dicyclohexyl-2,2'-[oxybis(methylene)]bis-2-propenoate and dibenzyl-2,2'-[oxybis(methylene)]bis-2-propenoate are preferred. These ether dimers may be used either alone or in combination of two or more thereof. A structure derived from the compound represented by the above general formula (ED) may be copolymerized with other monomers.

Among them, a (meth)acrylic resin having an allyl group or a vinyl ester group and a carboxyl group in the side chain thereof, an alkali-soluble resin having a double bond in the side chain thereof, described in Japanese Patent Application Laid-Open Nos. 2000-187322 and 2002-62698, or an alkali-soluble resin having an amide group in the side chain thereof, described in Japanese Patent Application Laid-Open No. 2001-242612 is suitable due to excellent balance of the film strength, the sensitivity and the developability.

Urethane-based binder polymers having an acid group, described in Japanese Patent Publication Nos. H7-12004, H7-120041, H7-120042, H8-12424 and S63-287944, Japanese Patent Application Laid-Open Nos. S63-287947, S63-287947 and H1-271741, and the like, or urethane-based binder polymers having an acid group and a double bond in the side chain thereof, described in Japanese Patent Application Laid-Open No. 2002-107918 has extremely excellent strength, and therefore, is advantageous from the viewpoint of the film strength.

Acetal-modified polyvinyl alcohol-based binder polymers having an acid group, described in European Patent No. 993966, European Patent No. 1204000, Japanese Patent Application Laid-Open No. 2001-318463 and the like have excellent film strength, and therefore, are suitable.

Polyvinyl pyrrolidone, polyethylene oxide and the like are useful as a water-soluble linear organic polymer. Alcohol-soluble nylon, polyether of 2,2-bis(4-hydroxyphenyl)-propane with epichlorohydrin, and the like are also useful so as to increase the strength of the cured film.

The weight average molecular weight of the binder polymer that may be used in the curable composition of the present invention (a polystyrene converted value measured by a GPC method) is preferably 5,000 or more and more preferably in the range of from 10,000 to 300,000, and the number average molecular weight thereof is preferably 1,000 or more and more preferably in the range of from 2,000 to 250,000. The polydispersity (weight average molecular weight/number average molecular weight) thereof is preferably 1 or more and more preferably in the range of from 1.1 to 10.

The binder polymer may be any one of a random polymer, a block polymer, a graft

polymer and the like.

The binder polymer that may be used in the present invention may be synthesized by a method known in the related art. Examples of solvents used in the synthesis include tetrahydrofuran, ethylene dichloride, cyclohexanone, methyl ethyl ketone, acetone, methanol, ethanol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 2-methoxyethyl acetate, diethylene glycol dimethyl ether, 1-methoxy-2-propanol, 1-methoxy-2-propylacetate, N,N-dimethyl formamide, N,N-dimethyl acetamide, toluene, ethyl acetate, methyl lactate, ethyl lactate, dimethyl sulfoxide, water and the like. These adhesives may be used either alone or in combination of two or more thereof.

Examples of the radical polymerization initiator used in the synthesis of the binder polymer that may be used in the curable composition of the present invention include compounds known in the related art, such as an azo initiator and a peroxide initiator.

In the curable composition of the present invention, the binder polymer may be used either alone or in combination of two or more thereof.

The curable composition of the present invention may or may not contain the binder polymer, but when the composition contains the binder polymer, the content of the binder polymer is preferably from 1 mass% to 40 mass%, more preferably from 3 mass% to 30 mass%, and even more preferably from 4 mass% to 20 mass%, based on the total solid content of the curable composition.

[Surfactant]

Various surfactants may be added to the curable composition of the present invention from the viewpoint of improving the coatability thereof. Various surfactants such as fluorine-based surfactants, nonionic surfactants, cationic surfactants, anionic surfactants and silicon-based surfactants may be used as the surfactant.

In particular, when the curable composition of the present invention contains a fluorine-based surfactant, and therefore, is prepared into a coating solution, liquid characteristics (in particular, fluidity) may be further improved, thus resulting in further improvements in uniformity of a coating thickness or liquid saving.

That is, when a film is formed by using a coating solution in which a photosensitive transparent composition containing a fluorine-based surfactant is applied, wettability into a surface to be coated is improved by reducing the interfacial tension between the surface to be coated and the coating solution, thereby improving the coatability into the surface to be coated. Accordingly, it is effective in that the formation of a uniform-thickness film with less

thickness unevenness may be more suitably carried out, even when a thin film having a thickness of several μm is formed with a small amount of the liquid.

The content by percent of fluorine in the fluorine-based surfactant is suitably from 3 mass% to 40 mass%, more preferably from 5 mass% to 30 mass%, and particularly preferably from 7 mass% to 25 mass%. The fluorine-based surfactant having a fluorine content by percent, which falls within the above-described range, is effective from the viewpoint of the thickness uniformity of the coating film and the liquid saving, and also exhibits good solubility in the curable composition.

Examples of the fluorine-based surfactant include MEGAFAC F171, MEGAFAC F172, MEGAFAC F173, MEGAFAC F176, MEGAFAC F177, MEGAFAC F141, MEGAFAC F142, MEGAFAC F143, MEGAFAC F144, MEGAFAC R30, MEGAFAC F437, MEGAFAC F475, MEGAFAC F479, MEGAFAC F482, MEGAFAC F554, MEGAFAC F780, and MEGAFAC F781 (all manufactured by DIC corporation), Fluorad FC430, Fluorad FC431, and Fluorad FC171 (all manufactured by Sumitomo 3M Limited), 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 SC393, and Surflon KH-40 (all manufactured by ASAHI GLASS CO. LTD.), PF636, PF656, PF6320, PF6520, PF7002 (all manufactured by OMNOVA) and the like.

Specific examples of the nonionic surfactant include glycerol, trimethylolpropane, trimethylolethane and ethoxylate thereof, propoxylate (for example, glycerol propoxylate, glycerin ethoxylate and the like), polyoxyethylene laurylether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene nonylphenyl ether, polyethylene glycol dilaurate, polyethylene glycol distearate, sorbitan fatty acid ester (Pluronic L10, L31, L61, L62, 10R5, 17R2, 25R2, and Tetronic 304, 701, 704, 901, 904, 150R1, which are manufactured by BASF Corporation, SOLSPERSE 20000 (manufactured by The Lubrizol Corporation), and the like.

Specific examples of the cationic surfactant include phthalocyanine derivatives (product name: EFKA-745, manufactured by Morishita & Co., Ltd.), organosiloxane polymer KP341 (manufactured by Shin-Etsu Chemical Co., Ltd.), (meth)acrylic acid-based copolymer Polyflow No. 75, No. 90, and No. 95 (manufactured by KYOEISHA CHEMICAL Co., Ltd.), W001 (manufactured by YUSHO CO., LTD.), and the like.

Specific examples of the anionic surfactant include W004, W005, W017 (manufactured by YUSHO CO., LTD.), and the like.

Examples of the silicon-based 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”, which are manufactured by Dow Corning Toray Co., Ltd., “TSF-4440”, “TSF-4300”, “TSF-4445”, “TSF-4460” and “TSF-4452”, which are manufactured by Momentive Performance Materials Inc., “KP341”, “KF6001” and “KF6002”, which are manufactured by Shin-Etsu Silicone Co., Ltd., “BYK307”, “BYK323” and “BYK330”, which are manufactured by BYK Chemie GmbH, and the like.

The surfactants may be used either alone or in combination of two or more thereof.

The curable composition may or may not contain the surfactant, but when the composition contains the surfactant, the amount of the surfactant added is preferably from 0.001 mass% to 2.0 mass% and more preferably from 0.005 mass% to 1.0 mass%, based on the total mass of the curable composition.

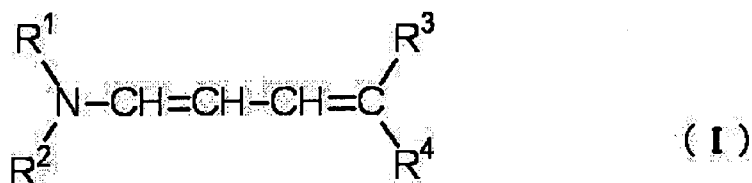
[Other Additives]

In order to improve physical properties of the cured film, known additives such as a plasticizer and a sensitization agent may be added to the curable composition.

Examples of the plasticizer include dioctyl phthalate, didodecyl phthalate, triethylene glycol dicaprylate, dimethylglycol phthalate, tricresyl phosphate, dioctyl adipate, dibutyl sebacate, triacetyl glycerin, and the like, and when a binder polymer is used, the plasticizer in an amount of 10 mass% or less may be added based on the total mass of the polymerizable compound and the binder polymer.

[UV Absorber]

The curable composition of the present invention may contain an UV absorber. As the UV absorber, a compound represented by the following general formula (I), which is a conjugated diene compound, is particularly preferred.



In the general formula (I), each of R¹ and R² independently represents a hydrogen atom, an alkyl group having from 1 to 20 carbon atoms, or an aryl group having from 6 to 20 carbon atoms, and R¹ and R² may be the same as or different from each other, but represents a hydrogen atom at the same time in no case.

Examples of the alkyl group having from 1 to 20 carbon atoms, represented by R^1 and R^2 include a methyl group, an ethyl group, a propyl group, an n-butyl group, an n-hexyl group, a cyclohexyl group, an n-decyl group, an n-dodecyl group, an n-octadecyl group, an eicosyl group, a methoxyethyl group, an ethoxypropyl group, a 2-ethylhexyl group, a hydroxyethyl group, a chloropropyl group, an N,N-diethylaminopropyl group, a cyanoethyl group, a phenethyl group, a benzyl group, a p-t-butylphenethyl group, a p-t-octylphenoxyethyl group, a 3-(2,4-di-t-amylphenoxy)propyl group, an ethoxycarbonylmethyl group, a 2-(2-hydroxyethoxy)ethyl group, a 2-furylethyl group and the like, and a methyl group, an ethyl group, a propyl group, an n-butyl group and an n-hexyl group are preferred.

The alkyl group represented by R^1 and R^2 may have a substituent group, and examples of the substituent group of the alkyl group having a substituent group include an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an acyloxy group, a halogen atom, an acylamino group, an acyl group, an alkylthio group, an arylthio group, a hydroxyl group, a cyano group, an alkyloxycarbonyl group, an aryloxycarbonyl group, a substituted carbamoyl group, a substituted sulfamoyl group, a nitro group, a substituted amino group, an alkylsulfonyl group, an arylsulfonyl group and the like.

The aryl group having from 6 to 20 carbon atoms, which is represented by R^1 and R^2 , may be a monocyclic or condensed cyclic ring, and may be any of a substituted aryl group having a substituent group, and an unsubstituted aryl group. Examples thereof include a phenyl group, a 1-naphthyl group, a 2-naphthyl group, an anthryl group, a phenanthryl group, an indenyl group, an acenabutenyl group, a fluorenyl group and the like. Examples of the substituent group of the substituted aryl group having a substituent group include an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an acyloxy group, a halogen atom, an acylamino group, an acyl group, an alkylthio group, an arylthio group, a hydroxyl group, a cyano group, an alkyloxycarbonyl group, an aryloxycarbonyl group, a substituted carbamoyl group, a substituted sulfamoyl group, a nitro group, a substituted amino group, an alkylsulfonyl group, an arylsulfonyl group and the like. Among them, a substituted or unsubstituted phenyl group, a 1-naphthyl group and a 2-naphthyl group are preferred.

R^1 and R^2 may form a cyclic amino group with a nitrogen atom to which R^1 and R^2 are bonded. Examples of the cyclic amino group include a piperidino group, a morpholino group, a pyrrolidino group, a hexahydroazepino group, a piperazino group and the like.

Among them, each of R^1 and R^2 is preferably a lower alkyl group having from 1 to 8 carbon atoms (for example, methyl, ethyl, isopropyl, butyl, sec-butyl, tert-butyl, pentyl,

tert-pentyl, hexyl, octyl, 2-ethylhexyl, tert-octyl and the like), or a substituted or unsubstituted phenyl group (for example, a tolyl group, a phenyl group, an anisyl group, a mesityl group, a chlorophenyl group, a 2,4-di-t-amylphenyl group and the like). It is also preferred that R^1 and R^2 are bonded to each other to form a ring containing the nitrogen atom represented by N in the formula (for example, a piperidine ring, a pyrrolidine ring, a morpholine ring and the like).

In the general formula (I), each of R^3 and R^4 represents an electron-attractive group. Here, the electron-attractive group is an electron-withdrawing group having a Hammett's substituent constant, σ_p value (hereinafter, simply referred to as " σ_p value") of from 0.20 to 1.0. The electron attractive group is preferably an electron-withdrawing group having a σ_p value of from 0.30 to 0.8.

Hammett's rule is an empirical rule proposed by L. P. Hammett in 1935 in order to quantitatively discuss the influence of substituent groups exerted on the reaction or equilibrium of a benzene derivative, and the validity of this rule is widely recognized today. The substituent constant determined by Hammett's rule includes the σ_p value and the σ_m value, and these values are disclosed in many general textbooks, the details of which are described in, for example, J. A. Dean, Ed., "Lange's Handbook of Chemistry", 12th Edition, 1979 (McGraw-Hill) or "Realms of Chemistry", No. 122, pp. 96 to 103, 1979 (Nankodo Co., Ltd.), and Chemical Reviews, Vol. 91, pp. 165 to 195, 1991. In the present invention, it is not meant that the values described in these textbooks and already known in the literature are not limited only to a certain substituent group, and even if the value is not known in the literature, the value will be definitely included in the present invention as long as the value falls within the range when measured on the basis of Hammett's rule.

Specific examples of the electron-withdrawing group having a σ_p value of from 0.20 to 1.0 include an acyl group, an acyloxy group, a carbamoyl group, an alkyloxycarbonyl group, an aryloxycarbonyl group, a cyano group, a nitro group, a dialkylphosphono group, a diarylphosphono group, a diarylphosphino group, an alkylsulfinyl group, an arylsulfinyl group, an alkylsulfonyl group, an arylsulfonyl group, a sulfonyloxy group, an acylthio group, a sulfamoyl group, a thiocyanate group, a thiocarbonyl group, an alkyl group substituted with at least two or more halogen atoms, an alkoxy group substituted with at least two or more halogen atoms, an aryloxy group substituted with at least two or more halogen atoms, an alkylamino group substituted with at least two or more halogen atoms, an alkylthio group substituted with at least two or more halogen atoms, an aryl group substituted with another

electron-withdrawing group having a σ_p value of 0.20 or more, a heterocyclic group, a chlorine atom, a bromine atom, an azo group, or a selenocyanate group. Among these substituent groups, groups capable of further having substituent groups may further have substituent groups such as those mentioned above.

Among them, each of R^3 and R^4 is preferably an acyl group, a carbamoyl group, an alkyloxycarbonyl group, an aryloxycarbonyl group, a cyano group, a nitro group, an alkylsulfonyl group, an arylsulfonyl group, a sulfonyloxy group and a sulfamoyl group, and particularly preferably an acyl group, a carbamoyl group, an alkyloxycarbonyl group, an aryloxycarbonyl group, a cyano group, an alkylsulfonyl group, an arylsulfonyl group, a sulfonyloxy group and a sulfamoyl group.

Among those described above, in the present invention, R^3 is preferably a group selected from a cyano group, $-\text{COOR}^5$, $-\text{CONHR}^5$, $-\text{COR}^5$ and $-\text{SO}_2\text{R}^5$, and R^4 is preferably a group selected from a cyano group, $-\text{COOR}^6$, $-\text{CONHR}^6$, $-\text{COR}^6$ and $-\text{SO}_2\text{R}^6$. Each of R^5 and R^6 independently represents an alkyl group having from 1 to 20 carbon atoms, or an aryl group having from 6 to 20 carbon atoms. The alkyl group having from 1 to 20 carbon atoms and the aryl group having from 6 to 20 carbon atoms, which are represented by R^5 and R^6 , have the same meaning as in R^1 and R^2 , respectively, and have the same preferred aspects.

R^3 and R^4 may be bonded to each other to form a ring.

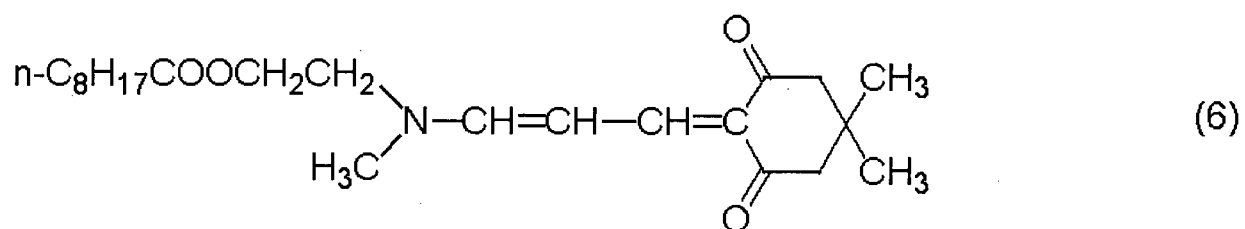
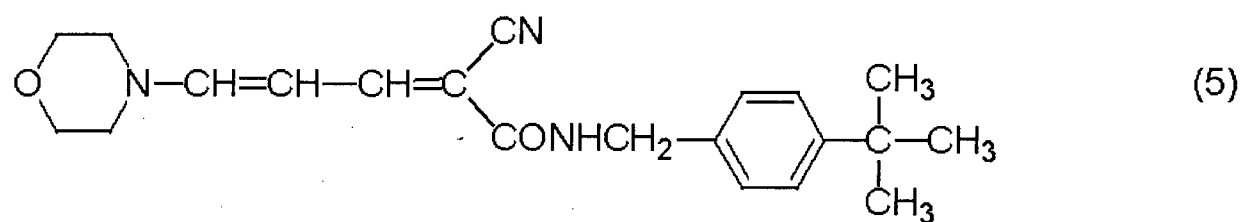
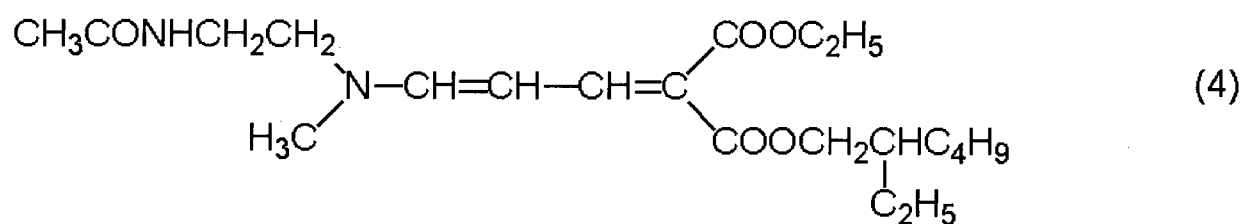
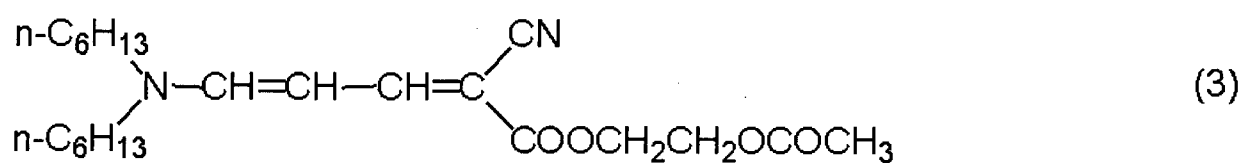
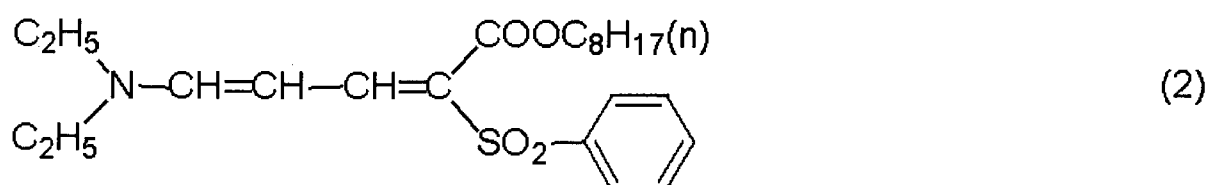
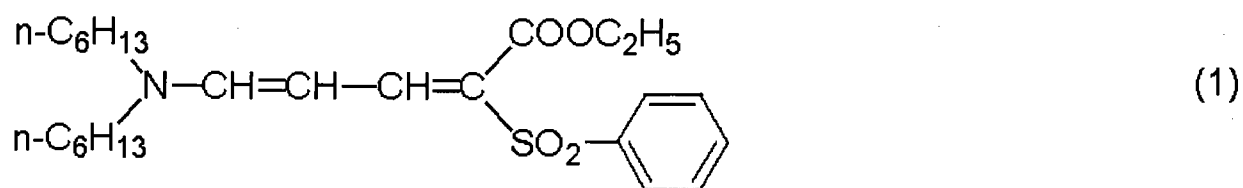
At least one of R^1 , R^2 , R^3 and R^4 may be in the form of a polymer derived from a monomer which is bonded to a vinyl group via a linking group. A copolymer with other monomers may be used. In the case of a copolymer, examples of the other monomer include acrylic acid, α -chloroacrylic acid, α -aracrylic acid (for example, an ester derived from acrylic acids such as methacrylic acid, preferably a lower alkyl ester and amide, for example, acrylamide, methacrylamide, t-butylacrylamide, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-propylacrylate, n-butylacrylate, 2-ethylhexylacrylate, n-hexylacrylate, octyl methacrylate and lauryl methacrylate, methylenebisacrylamide and the like), a vinyl ester (for example, vinyl acetate, vinyl propionate, vinyl laurate and the like), acrylonitrile, methacrylonitrile, an aromatic vinyl compound (for example, styrene and the derivatives thereof, for example, vinyltoluene, divinylbenzene, vinylacetophenone, sulfostyrene, styrenesulfinic acid and the like), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, a vinyl alkyl ether (for example, vinyl ethyl ether and the like), maleic acid ester, N-vinyl-2-pyrrolidone, N-vinylpyridine, 2- and 4-vinylpyridine and the like.

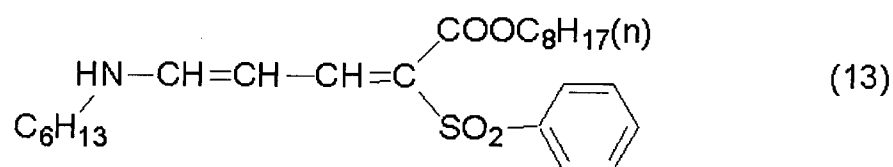
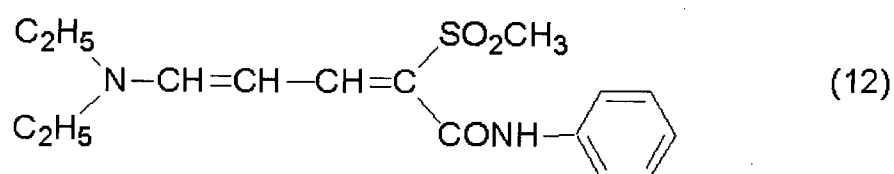
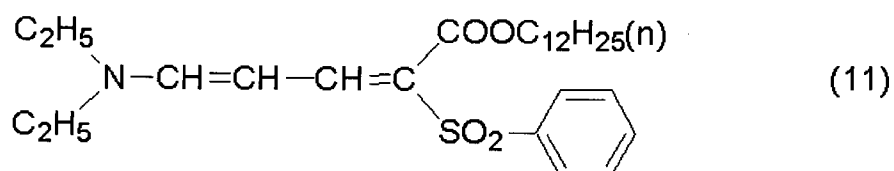
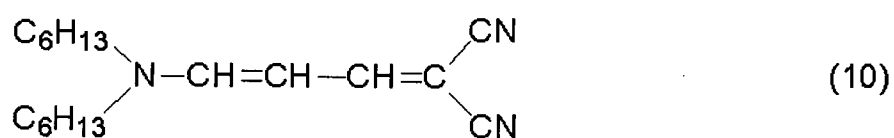
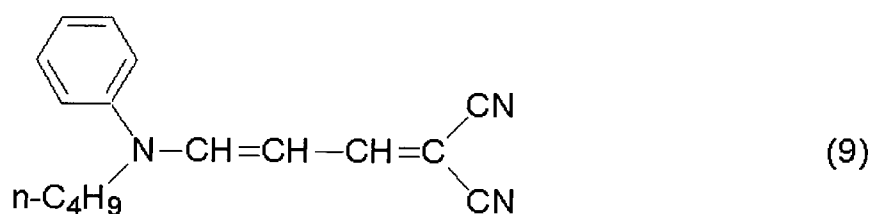
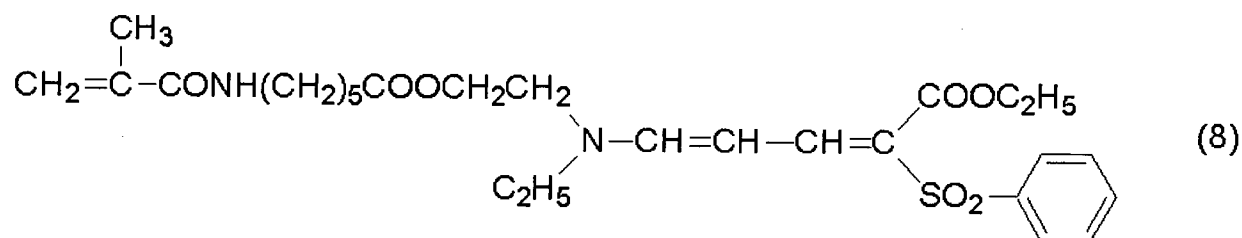
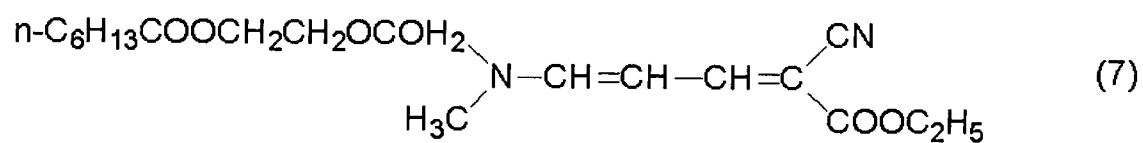
Among them, an acrylic acid ester, a methacrylic acid ester and an aromatic vinyl

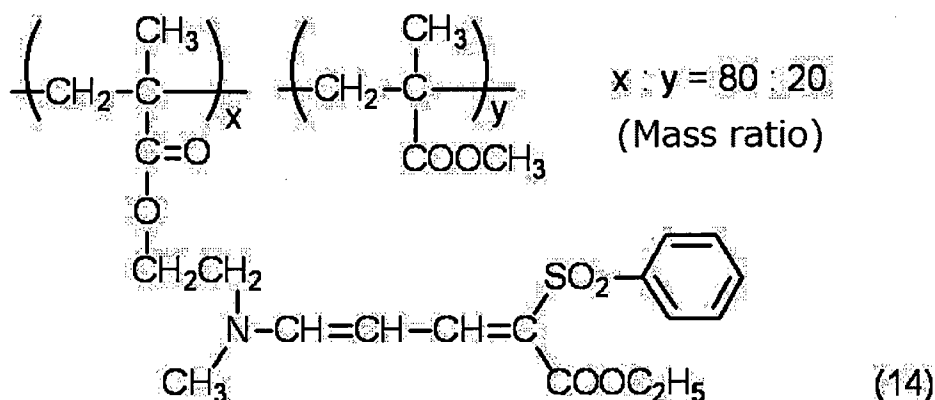
compound are particularly preferred.

Two or more kinds of the other monomer compounds may be used in combination. For example, n-butyl acrylate and divinylbenzene, styrene and methyl methacrylate, methyl acrylate and methacrylate acid, and the like may be used in combination.

Hereinafter, preferred specific examples [exemplary compounds (1) to (14)] of the compound represented by the above general formula (I) will be set forth. However, the present invention is not limited thereto.







The UV absorber represented by the general formula (I) may be synthesized by the methods described in Japanese Patent Publication No. S44-29620, Japanese Patent Application Laid-Open Nos. S53-128333, S61-169831, S63-53543, S63-53544 and S63-56651, and the like, and a pamphlet of WO2009/123109. Specifically, the exemplary compound (1) may be synthesized by a method described in paragraph number 0040 of a pamphlet of WO2009/123109.

The curable composition of the present invention may or may not contain an UV absorber, but when the composition contains an UV absorber, the content of the UV absorber is preferably from 0.1 mass% to 10 mass%, more preferably from 0.1 mass% to 5 mass% and particularly preferably from 0.1 mass% to 3 mass%, based on the total solid content of the composition.

In the present invention, the various UV absorbers may be used either alone or in combination of two or more thereof.

It is preferred that the curable composition of the present invention is filtered by a filter, for the purpose of removing impurities or reducing defects. Filters that have been used in the related art for filtration use and the like may be used without any particular limitation. Examples thereof include filters formed of a fluorine resin such as polytetrafluoroethylene (PTFE), a polyamide-based resin such as Nylon-6 and Nylon-6,6, and a polyolefin resin (including high density and ultrahigh molecular weight) such as polyethylene and polypropylene (PP). Among these materials, polypropylene (including high density polypropylene) is preferred.

As a pore diameter of the filter, it is preferably about from 0.01 μm to 7.0 μm , preferably about from 0.01 μm to 2.5 μm and more preferably about from 0.01 μm to 1.5 μm . By adjusting the diameter to this range, it is possible to certainly remove fine impurities which are incorporated into the dissolved pigment and the like to suppress the preparation of uniform

and smooth curable composition in the subsequent process.

When a filter is used, other filters may be combined. At that time, filtering at a first filter may be performed once or two or more times. When other filters are combined to perform filtering two or more times, it is preferred that a pore diameter at a second filtering or after a second filtering is bigger than a pore diameter at a first filtering. First filters having different pore diameters within the above-described range may be combined. As the pore diameter herein, a reference may be made to nominal values of a filter maker. As a commercially available filter, one selected from various filters provided by, for example, Nihon Pall Corporation, Advantech Toyo Roshi Kaisha, Ltd., Nihon Entegris, Inc. (formerly Nippon Microlith Co. Ltd.), KITZ MICRO FILTER CORPORATION and the like may be used.

As a second filter, a filter formed of a material which is the same as the material for the above-described first filter and the like may be used. The second filter suitably has a pore diameter of about from 0.5 μm to 7.0 μm , preferably about from 2.5 μm to 7.0 μm and more preferably about from 4.5 μm to 6.0 μm . By setting the pore diameter within this range, while remaining component particles contained in a mixed liquid, impurities which are incorporated into the mixed liquid and suppress the preparation of uniform and smooth curable composition in the subsequent process may be removed.

For example, the filtering at the first filter may be performed with only a liquid dispersion, and the second filtering may be performed after other components are mixed.

[Method for Manufacturing Transparent Film]

A method for manufacturing a transparent film of the present invention includes a process of coating the curable composition described above on a wafer by means of a spray method, a roll coat method, a spin coating method, a bar-coating method and the like, a subsequent first heating process, and a subsequent second heating process at a temperature higher than the heating temperature.

The conditions in the first heating process are the same as the conditions as described below as pre-bake conditions in the (I) process in the method for manufacturing a microlens.

The conditions in the second heating process are the same as the conditions as described below as post-bake conditions in the (IV) process in the method for manufacturing a microlens.

<Microlens>

The curable composition of the present invention may form a transparent film which has a high refractive index and high transmittance, and thus, may be very suitably used for forming, for example, a microlens and a microlens array.

That is, the curable composition of the present invention is preferably for forming a microlens.

The present invention also relates to a microlens formed by using a transparent film formed by using the curable composition of the present invention.

[Method for Forming Microlens]

As a method for manufacturing a microlens by using the curable composition of the present invention, a method which is usually used may be applied without any particular limitation, and examples thereof include a manufacturing method further including a process of subjecting the transparent film described above to post-bake treatment to shape the transparent film and a dry etching process and the like.

The process of subjecting the transparent film to post-bake treatment to shape the transparent film is the same as the process to be described in detail below as the (f) process.

The dry etching process is the same as the process to be described in detail below as the (g) process.

As a preferred aspect of the method for manufacturing a microlens by using the curable composition of the present invention, examples thereof include a manufacturing method, at least including the following (I) to (IV) processes.

(I) A process of forming a coating film of the curable composition of the present invention on a substrate

(II) A process of irradiating radiation on at least some portion of the coating film

(III) A process of developing the coating film after the irradiation

(IV) A process of heating the coating film after the development

Hereinafter, these processes will be described.

(I) Process

In this process, the curable composition is preferably coated as a liquid composition on the surface of a substrate and subjected to pre-bake to remove the solvent, thereby forming a coating film on the substrate.

Examples of the substrate include a glass substrate, a silicon wafer, a substrate with various metal layers formed on the surface thereof, a substrate on which an on-chip color filter

for an image sensor is coated, and the like.

The coating method is not particularly limited, and an appropriate method such as, for example, a spray method, a roll coat method, a spin coating method and a bar-coating method may be employed.

The pre-bake condition may vary according to the kind or use amount of each component, but is usually at from 60°C to 120°C for about from 30 sec to 15 min. The film thickness of the coating film to be formed is a value after the pre-bake, and is preferably about from 0.5 μm to 20 μm .

(II) Process

In this process, radiation is irradiated on at least some portion of the coating film formed.

When radiation is irradiated only on some portion of the coating film, the radiation is irradiated via a mask having a predetermined pattern.

As the radiation rays to be irradiated, ultraviolet rays such as, for example, g-ray and i-ray, far ultraviolet rays such as KrF excimer laser and ArF excimer laser, X-ray such as synchrotron radiation, charged particle radiations such as electron radiation may be used, but among them, ultraviolet rays are most preferred.

The exposure amount may be suitably selected according to the constitution of a curable composition and the like, but is preferably about from 50 mJ/cm^2 to 2,000 mJ/cm^2 .

(III) Process

In this process, the coating film after the exposure is developed by a developing solution, preferably an alkaline developing solution and a pattern of a predetermined shape is formed by removing unirradiated portions, of radiations.

Examples of the alkaline developing solution include an aqueous solution of sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium metasilicate, ammonia, ethylamine, n-propylamine, diethylamine, diethylamino ethanol, di-n-propylamine, triethyl amine, methyldiethyl amine, dimethyl ethanolamine, triethanol amine, tetramethyl ammonium hydroxide, tetraethyl ammonium hydroxide, pyrrole, piperidine, 1,8-diazabicyclo[5,4,0]-7-undecene, 1,5-diazabicyclo[4.3.0]-5-nonene and the like. A water-soluble organic solvent such as methanol and ethanol, a surfactant, or various organic solvents may be added to the alkaline developing solution and used.

As a development method, an appropriate method such as an adhesion method, a dipping method, a rocking immersion method and a showering method may be employed. Meanwhile, after being developed by the alkaline developing solution, the coating film is generally washed by, for example, running water.

Development time varies according to the composition of the photosensitive resin composition and the composition of the developing solution, but is usually about from 30 to 120 sec at room temperature.

(IV) Process

In this process, the coating film is cured by heating (post-bake) the coating film after the development by using a heating apparatus such as a hot plate and an oven.

In the post-bake, the heating temperature is usually from 120°C to 250°C, and preferably from 160°C to 230°C. The heating time may vary according to the heating means, but when heating is performed on a hot plate, the heating time is usually about from 5 min to 30 min, and when the heating is performed in an oven, the heating time is usually about from 30 min to 90 min.

In performing the post-bake, a step bake method including carrying out a heat treatment two or more times may be employed.

As another preferred aspect of the method for manufacturing a microlens by using the curable composition of the present invention, examples thereof include a forming method, at least including the following (a) to (g) processes.

(a) A process of forming a coating film on a substrate such as a color filter by using the curable composition of the present invention

(b) A process of performing at least one of heating the above-described coating film to dry (or dry and cure) the coating film or exposing the above-described coating film by means of a light source (g-ray, i-ray and the like) having an appropriate wavelength to cure the coating film, thereby obtaining a high refractive index film (transparent film)

(c) A process of forming a resist coating film on the high refractive index film after the heating

(d) A process of exposing the resist coating film by using a light source (g-ray, i-ray and the like) having an appropriate wavelength

(e) A process of developing the resist coating film after the exposure to form a resist pattern

(f) A process of shaping the resist pattern into a lens-type by means of post-heating

(g) A process of removing the resist pattern and some portion of the high refractive index film by means of dry etching to shape the high refractive index film into a lens-type

Hereinafter, these processes will be described.

- (a) Process -

In this process, the curable composition of the present invention is coated on a substrate such as a color filter to form a coating film.

Examples of the coating method include the method as in the process (I).

- (b) Process -

In this process, a preferred embodiment of heating the coating film may include a two-step heating treatment of pre-bake and post-bake.

The pre-bake condition may vary according to the kind or use amount of each component, but is usually at from 60°C to 120°C for about from 30 sec to 15 min. The film thickness of the coating film to be formed is a value after the pre-bake, and is preferably about from 0.5 μm to 20 μm . The pre-bake process may be omitted in some cases.

Subsequently, the coating film is cured by heating (post-bake) the coating film using a heating apparatus such as a hot plate and an oven. The post-bake condition is usually at from 120°C to 300°C for about from 30 sec to 60 min. Meanwhile, the curing may be promoted by performing exposure prior to the post-bake process.

When the above-described coating film is exposed by a light source (g-ray, i-ray and the like) having an appropriate wavelength to be cured, the kind of radiation and the amount of exposure, which are the same as in the process (II), may be applied to the radiation to be irradiated.

- (c) Process -

In the process, a resist coating film is formed on a high refractive index film. As the resist, generally commercially available resists which is able to form a pattern by ultraviolet exposure may be used. For the resist coating film, the pre-bake is performed in the (a) process.

- (d) Process -

In this process, (the coating film is exposed into a pattern type by using a mask. The kind of radiation and the amount of exposure, which are the same as in the process (II), may be applied to the radiation to be irradiated.

- (e) Process -

In this process, the resist coating film after the exposure is developed by a developing solution, preferably an alkaline developing solution and a pattern of a predetermined shape is formed by removing unirradiated portions or irradiated portions, of the radiation.

Examples of the alkaline developing solution include the alkaline developing solution as in the process (III).

Examples of the developing method include the method as described above about the process (III).

The developing time is the same as what is described above in the process (III).

- (f) Process -

In this process, a post-heating (post-bake) is performed by a heating apparatus such as a hot plate and an oven, thereby shaping the resist into a lens type after the pattern is formed. The post-bake condition is usually at from 120°C to 300°C for about from 30 sec to 60 min. For shaping into a lens type, a step bake method including carrying out a heat treatment two or more times may also be employed.

- (g) Process -

Dry etching may be performed by a known method (for example, Japanese Patent Application Laid-Open No. 2010-204154).

In this manner, a desired microlens may be manufactured.

According to the method of the present invention for manufacturing a microlens, a high-definition microlens and microlens array having excellent properties (for example, high refractive index and high transmittance) may be simply formed with a high product yield.

The microlens in the present invention is formed from the curable composition of the present invention and has excellent balance in properties, and may be very suitably used in a liquid crystal display device for various OA equipment, liquid crystal televisions, portable telephones, projectors and the like, the imaging optics of a on-chip color filter such as a facsimile, an electronic copy machine, a solid-state image sensing device and the like, an optical fiber connector, and the like.

<Solid-State Image Sensing Device>

The solid-state image sensing device of the present invention includes the microlens formed by using the above-described curable composition of the present invention.

The solid-state image sensing device of the present invention includes a microlens which has a high refractive index and high transmittance, and thus, noise may be reduced, and

excellent color reproducibility is shown.

The solid-state image sensing device of the present invention is not particularly limited as long as the device has a constitution in which the microlens formed by using the curable composition of the present invention is included and a constitution which functions as a solid-state sensing device, and examples thereof include a constitution in which a light-receiving element consisting of a plurality of photodiodes, polysilicons and the like which constitute a light-receiving area of a solid-state image sensing device (CCD image sensor, CMOS image sensor, and the like) is disposed on a substrate, a constitution in which the microlens is included on a color filter and the like.

The method of the present invention for manufacturing a solid-state image sensing device is not particularly limited, but as one preferred aspect, the method includes a process of forming red pixels, blue pixels and green pixels on a substrate for a solid-state image sensing device having at least a photodiode, a light-shielding film and a device protective film, a process of coating the curable composition described above and performing heating, a process of forming a resist pattern, a process of shaping a resist pattern formed by performing post-bake treatment into a lens-type shape, and a process of performing dry etching.

The process of coating the curable composition and performing heating is performed in the same manner as in the process of forming a coating film on a substrate and the process of heating the coating film to dry (or dry and cure) the coating film in the (a) process and the (b) process in the above-described method for manufacturing a microlens.

The process of forming a resist pattern is performed in the same manner as in the (d) process and (e) process in the above-described method for manufacturing a microlens.

The process of shaping a resist pattern formed by performing a post-bake treatment into a lens-type shape is performed in the same manner as in the (f) process in the above-described method for manufacturing a microlens.

The process of performing dry etching is performed in the same manner as in the (g) process in the above-described method for manufacturing a microlens.

Examples

Hereinafter, the present invention will be specifically described with reference to Examples, but the present invention is not limited to the Examples. Meanwhile, unless particularly specified, “parts” and “%” are by mass.

In the Examples, the acid value and the amine value were determined by a

potentiometric method (solvent tetrahydrofuran/water=100/10 (volume ratio), a volumetric solution 0.01 N sodium hydroxide aqueous solution (acid value) and 0.01 N hydrochloric acid (amine value)).

(Synthetic Example 1) Synthesis of Polyester (i-1)

6.4 g of n-octanoic acid, 200 g of ϵ -caprolactone and 5 g of Titanium (IV) tetrabutoxide were mixed, heated at 160°C for 8 hr, and then cooled to room temperature to obtain polyester (i-1).

The scheme is shown as follows.



(Synthetic Examples 2 to 15)

Polyesters of (i-2) to (i-10), and (i-15) to (i-19) were obtained in the same manner as in Synthetic Example 1, except that carboxylic acid and lactone in Synthetic Example 1 were changed as in Table 1 and the feed volume of carboxylic acid was changed. The number average molecular weights and weight average molecular weights of these resins obtained in the Synthetic Examples were measured by the GPC method which had already been described above. The results are shown in the following Table 1. The number of atoms calculated about each polyester and the number of units of lactone-derived repeating units calculated from the raw material feed ratio are shown together in the following Table 1.

Table 1

	Poly- ester	Carboxylic acid (Content: g)	Lactone	Weight average molecular weight	Number average molecular weight	Number of lactone-derived repeating units	Number of atoms
Synthetic Example 1	(i-1)	n-octanoic acid (6.4)	ϵ -capro- lactone	15,000	10,000	40	330
Synthetic Example 2	(i-2)	n-octanoic acid (12.6)	ϵ -capro- lactone	4,100	2,200	10	90
Synthetic Example 3	(i-3)	n-octanoic acid (5.1)	ϵ -capro- lactone	18,000	14,000	50	410
Synthetic Example 4	(i-4)	Palmitic acid (5.6)	ϵ -capro- lactone	25,000	16,500	80	658
Synthetic Example 5	(i-5)	Palmitic acid (7.5)	ϵ -capro- lactone	23,000	19,000	60	498
Synthetic Example 6	(i-6)	Decanoic acid (15.1),	ϵ -capro- lactone	8,000	5,500	20	172
Synthetic Example 7	(i-7)	12-hydroxy- stearic acid (17.5)	ϵ -capro- lactone	10,000	8,000	30	261
Synthetic Example 8	(i-8)	12-hydroxy- stearic acid (5.25)	δ -decano- lactone	30,000	21,000	100	1221
Synthetic Example 9	(i-9)	Ricinoleic acid (10.4)	ϵ -capro- lactone	19,000	14,000	50	421
Synthetic Example 10	(i-10)	2,2-bis(hyd- roxymethyl) butyric acid (6.5)	ϵ -capro- lactone	15,000	12,000	20	170
Synthetic Example 11	(i-15)	n-octanoic acid (50.5)	ϵ -capro- lactone	15,000	10,000	5	50
Synthetic Example 12	(i-16)	n-octanoic acid (16.8)	ϵ -capro- lactone	4,100	2,200	15	130
Synthetic Example 13	(i-17)	Palmitic acid (18.0)	ϵ -capro- lactone	18,000	14,000	25	218
Synthetic Example 14	(i-18)	Palmitic acid (3.7)	ϵ -capro- lactone	25,000	16,500	120	978
Synthetic Example 15	(i-19)	12-hydroxy- stearic acid (3.8)	ϵ -capro- lactone	23,000	19,000	150	1821

(Synthetic Example 16) Synthesis of Polyester (i-11)

100 g of 12-hydroxystearic acid, 0.1 g of titanium (IV) tetrabutoxide and 300 g of xylene were mixed under nitrogen stream and reacted with each other while water produced at an external temperature of 160°C was distilled off with a Dean-Stark tube. Heating was stopped at a point where the number average molecular weight and the weight average molecular weight in the GPC measurement were 8,000 and 12,000, respectively to obtain polyester (i-11).

(Synthetic Example 17) Synthesis of Polyester (i-12)

Experiment was performed in the same manner as in Synthetic Example 16 and the heating was stopped at a point where the number average molecular weight and the weight average molecular weight in the GPC measurement were 6,000 and 11,000, respectively to obtain polyester (i-12).

(Synthetic Example 18) Synthesis of Polyester (i-13)

307 g of adipic acid, 110 g of neopentyl glycol, 57 g of 1,4-butanediol and 26 g of ethylene glycol were reacted with each other under nitrogen stream while water produced at an external temperature of 160°C was distilled off with a Dean-Stark tube. Reaction was stopped at a point where the number average molecular weight and the weight average molecular weight in the GPC measurement were 8,000 and 13,000, respectively to obtain polyester (i-13).

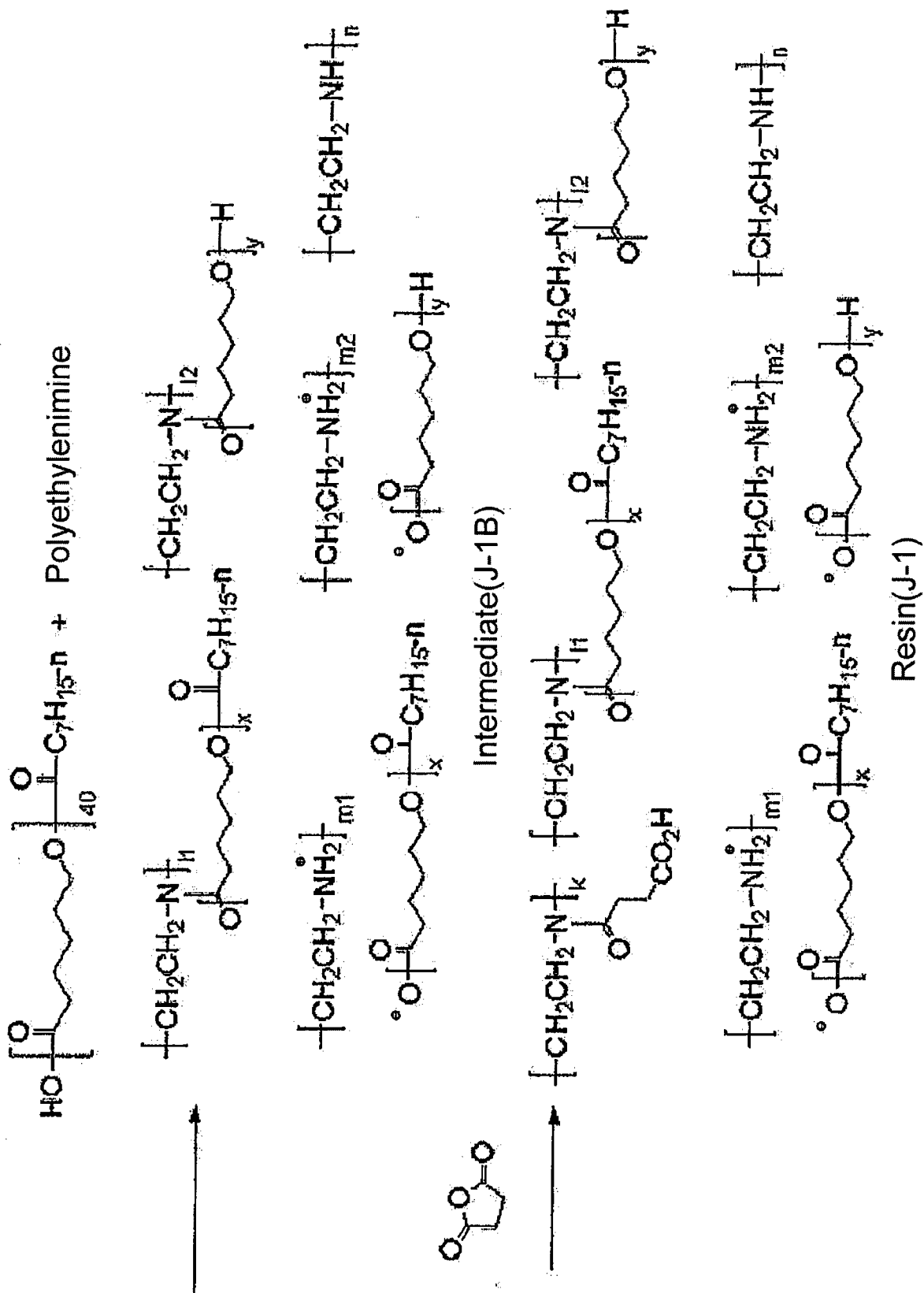
(Synthetic Example 19) Synthesis of Macro Monomer (i-14)

50 g (500 mmol) of methyl methacrylate, 100 g of propylene glycol monomethyl ether and 2.5 g (23.6 mmol) of 2-mercaptopropionic acid were heated to 80°C under nitrogen stream. Subsequently, 0.1 g of V-601 (azobis(isobutyric acid)dimethyl) manufactured by Wako Pure Chemical Industries, Ltd.) was added thereto, and 0.1 g of V-601 was also added thereto three hours later and heated for 4 hr. Thereafter, 3.35 g (23.6 mmol) of glycidyl methacrylate and 0.5 g of tetrabutyl ammonium bromide were added thereto and heated at 80°C for 5 hr. After being allowed to cool, a mixed solvent of 200 mL of water and 800 mL of methanol was used for reprecipitation, and then dried to obtain 55 g of a macro monomer (i-14).

(Synthetic Example 20) [Synthesis of Resin (J-1)]

10 g of polyethylene imine (SP-018, number average molecular weight 1,800, manufactured by NIPPON SHOKUBAI CO., LTD.) and 100 g of polyester (i-1) as a precursor y of Y were mixed and heated at 120°C for 3 hr to obtain an intermediate (J-1B). Thereafter, the intermediate was allowed to cool to 65°C and stirred for 2 hr while 200 g of propyleneglycol 1-monomethylether 2-acetate (hereinafter, referred to as PGMEA in some cases) containing 2.3 g of anhydrous succinic acid as a precursor x of X was slowly added thereto. Thereafter, PGMEA was added thereto to obtain a solution of PGMEA of the resin (J-1) in an amount of 10 mass%. The resin (J-1) contains a side chain derived from polyester (i-1) and a group having an anhydrous succinic acid-derived functional group (a carboxylic group) with a pKa of 14 or less.

The synthesis scheme is shown as follows.



The acid value titration of the intermediate (J-1 B) was performed, and thus it could be confirmed that the acid value was 6.4 mgKOH/g. The amine value titration and acid titration of the resin (J-1) were performed, and thus it was found that the acid value was 17.9 mgKOH/g and the amine value was 46.2 mgKOH/g. That is, the mol% of a repeating unit corresponding to the general formula (J-1) may be calculated from the difference between the acid value of the resin (J-1) and the acid value of the intermediate (J-1B), (l_1+l_2) (=mol% of a repeating unit corresponding to the general formula (I-2)) may be calculated from the difference between the amine value of the resin (J-1) and the number of nitrogen atoms of the resin before reaction, and (m_1+m_2) (= mol% of the a repeating unit corresponding to the general formula (I-3)) may be calculated from the acid value of the intermediate (J-1B). The result shows that $k/(l_1+l_2)/(m_1+m_2)/n=10/50/5/35$.

That is, it can be known that it is a resin including a repeating unit wherein X is $-\text{COCH}_2\text{CH}_2\text{CO}_2\text{H}$ in the repeating unit represented by the general formula (I-1) in an amount of 10 mol% and including a repeating unit wherein Y is poly(ϵ -caprolactone) in the repeating unit represented by the general formula (I-2) in an amount of 50 mol%. The weight average molecular weight as measured by the GPC method was 15,000.

(Synthetic Examples 21 to 32, and 47 to 52)

[Synthesis of Resins (J-2) to (J-13), and (J-28) to (J-33)]

Synthesis was performed in the same manner as in Synthetic Example 20 to obtain solutions of PGMEA of the resins (J-2) to (J-13), and (J-28) to (J-33) in an amount of 10 mass%, except that the amino group-containing resin, the precursor x of X and polyesters obtained in the Synthetic Examples 1 to 18 as described in Tables 2 to 4 were used. As the resin (J-13), a reaction solution was reprecipitated with water and dried to obtain a solution of PGMEA of the resin (J-13) in an amount of 10 mass%, and thus it was used.

The amino group-containing resins used in the synthesis are as follows.

SP-003 (polyethylene imine (manufactured by NIPPON SHOKUBAI CO., LTD.) number average molecular weight 300)

SP-006 (polyethylene imine (manufactured by NIPPON SHOKUBAI CO., LTD.) number average molecular weight 600)

SP-012 (polyethylene imine (manufactured by NIPPON SHOKUBAI CO., LTD.) number average molecular weight 1,200)

SP-018 (polyethylene imine (manufactured by NIPPON SHOKUBAI CO., LTD.)

number average molecular weight 1,800)

SP-200 (polyethylene imine (manufactured by NIPPON SHOKUBAI CO., LTD.)
number average molecular weight 10,000)

(Synthetic Example 33)

[Synthesis of Resin (J-14)]

In a reactor equipped with a Dean-Stark tube, 100 g of an aqueous solution of polyallylamine (PAA-08, weight average molecular weight 8,000, manufactured by NIPPON SHOKUBAI CO., LTD.) and 500 g of toluene were refluxed until the distillation of the moisture at an external temperature of 130°C is stopped, and then the mixture was concentrated to remove toluene. Subsequently, 100 g of polyester (i-1) was mixed to heat the resulting mixture at 120°C for 3 hr. Thereafter, the mixture was allowed to cool to 65°C, and 200 g of PGMEA including 9.0 g of anhydrous glutaric acid (precursor x of X) was slowly added thereto and stirred for 2 hr. Thereafter, PGMEA was added thereto to obtain a solution of PGMEA of the resin (J-14) in an amount of 10 mass%.

(Synthetic Examples 34 to 45, and 53 to 56)

[Synthesis of Resins (J-15) to (J-26), and (J-34) to (J-37)]

Synthesis was performed in the same manner as in Synthetic Example 33 to obtain solutions of PGMEA of the resins (J-15) to (J-26), and (J-34) to (J-37) in an amount of 10 mass%, except that the amino group-containing resin, the precursor x of X and polyesters obtained in the Synthetic Examples 1 to 18 as described in Tables 2 to 4 were used.

The amino group-containing resins used in the synthesis are as follows.

PAA-01 (polyallylamine (manufactured by Nitto Boseki Co., Ltd.) weight average molecular weight 1,000)

PAA-03 (polyallylamine (manufactured by Nitto Boseki Co., Ltd.) weight average molecular weight 3,000)

PAA-05 (polyallylamine (manufactured by Nitto Boseki Co., Ltd.) weight average molecular weight 5,000)

PAA-08 (polyallylamine (manufactured by Nitto Boseki Co., Ltd.) weight average molecular weight 8,000)

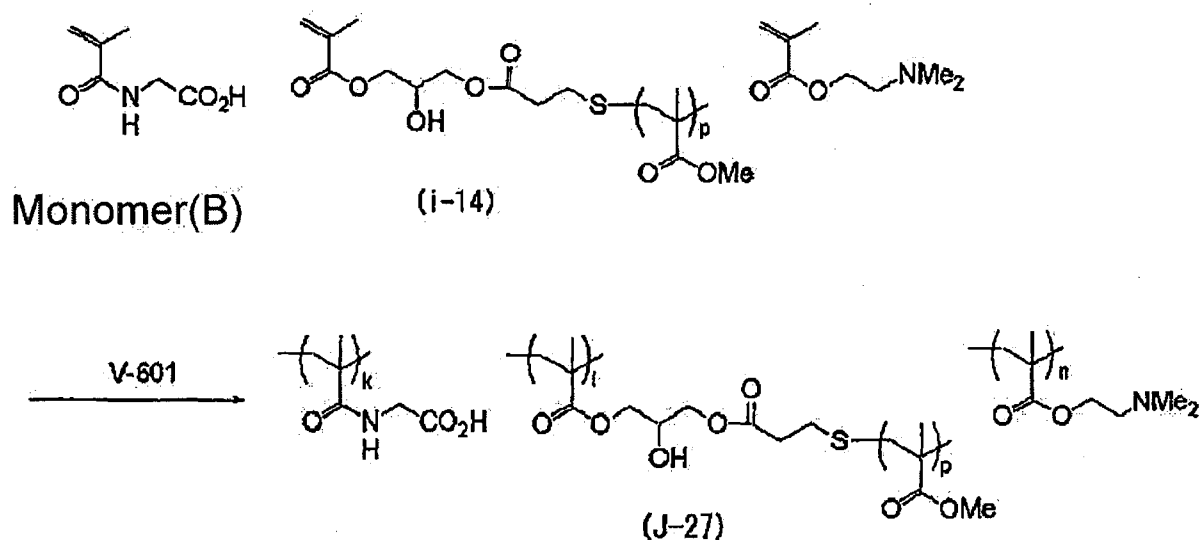
PAA-15 (polyallylamine (manufactured by Nitto Boseki Co., Ltd.) weight average molecular weight 15,000)

(Synthetic Example 46)

[Synthesis of Resin (J-27)]

0.50 g (3.5 mmol) of the monomer (B), 55 g (23 mmol) of the macro monomer (i-14), 1.50 g (9.6 mmol) of 2-(N,N-dimethylamino ethyl) methacrylate and 0.2 g (1.0 mmol) of dodecanethiol were dissolved in a mixed solvent of 200 g of dimethyl sulfoxide and 100 g of N-methyl pyrrolidone. After the mixture was heated to 80°C, 0.1 g of V-601 was added and stirred for 3 hr. Thereafter, 0.1 g of V-601 was added thereto, stirred for 3 hr, and then allowed to cool. The solution obtained was added dropwise to 4,000 L of water over 1 hr and the precipitated resin was collected by filtration. After drying, the resin was dissolved in 1-methoxy-2-propanol to obtain a solution in an amount of 10 mass%.

The synthesis scheme is shown as follows.



(Measurement of Acid Value and Amine Value)

The acid value and amine value of the obtained resins (J-1) to (J-37) were measured by the above-described method. The results were written along in Tables 2 to 4.

From these measurement results, it could be confirmed that a functional group having a pKa of 14 or less in the side chain thereof was present from the results of the acid value of the intermediate and the acid value of a target resin and the like.

Table 2

	Resin	Amino group-containing resin (g)	Polyester (g)	X precursor (g)	Acid value of intermediate (mgKOH/g)	Amine value of intermediate (mgKOH/g)	Acid value of target resin (mgKOH/g)	Amine value of target resin (mgKOH/g)	Weight average molecular weight
Synthetic Example 20	(J-1)	SP-018(10)	(i-1)(100)	Anhydrous succinic acid (2.3)	6.4	56.3	17.9	46.2	15000
Synthetic Example 21	(J-2)	SP-006(10)	(i-2)(100)	Anhydrous glutaric acid (1.2)	11.4	41.8	7.4	66.8	6000
Synthetic Example 22	(J-3)	SP-012(15)	(i-3)(100)	Anhydrous succinic acid (0.5)	4.9	85.5	7.9	84.1	17000
Synthetic Example 23	(J-4)	SP-006(10)	(i-4)(100)	Diketene (3.8)	6.5	62.4	21.9	45.1	12000
Synthetic Example 24	(J-5)	SP-200(5)	(i-5)(100)	Anhydrous succinic acid (3.0)	11.6	38.4	21.8	23.7	8000
Synthetic Example 25	(J-6)	SP-018(10)	(i-6)(100)	Butane sulfone (1.6)	8.2	49.6	17.5	41.4	32000
Synthetic Example 26	(J-7)	SP-018(10)	(i-7)(100)	Anhydrous cyclohexane carboxylic acid (1.8)	8.4	86.8	17.3	96.3	15000
Synthetic Example 27	(J-8)	SP-012(10)	(i-8)(100)	Anhydrous maleic acid (2.1)	6.3	75.3	19.2	51.4	18000
Synthetic Example 28	(J-9)	SP-006(5)	(i-9)(100)	Anhydrous succinic acid (1.5)	17.1	44.5	15.7	34.1	18000
Synthetic Example 29	(J-10)	SP-003(8)	(i-10)(100)	Anhydrous succinic acid (2.2)	2.6	70.2	14.6	61.3	18000
Synthetic Example 30	(J-11)	SP-006(14)	(i-11)(100)	Anhydrous cyclohexane carboxylic acid (1.8)	11.7	87.2	23.4	76.5	18000
Synthetic Example 31	(J-12)	SP-012(10)	(i-12)(100)	Acrylic acid (2.1)	6.5	58.3	16.2	47.3	18000
Synthetic Example 32	(J-13)	SP-006(10)	(i-13)(100)	Anhydrous succinic acid (2.2)	12.1	55.7	27.4	37.4	18000
Synthetic Example 33	(J-14)	PAA-08(15)	(i-1)(100)	Anhydrous glutaric acid (9.0)	6.5	46.3	41.5	11.5	18000
Synthetic Example 34	(J-15)	PAA-15(15)	(i-2)(100)	Diketene (4.3)	6.3	34.6	26.1	11.9	18000

Table 3

	Resin	Amino group-containing resin (g)	Polyester	X precursor (g)	Acid value of intermediate (mgKOH/g)	Amine value of intermediate (mgKOH/g)	Acid value of target resin (mgKOH/g)	Amine value of target resin (mgKOH/g)	Weight average molecular weight
Synthetic Example 35	(J-16)	PAA-15(10)	(i-3)(100)	Anhydrous succinic acid (3.2)	8.1	42.6	24.6	28.5	15000
Synthetic Example 36	(J-17)	PAA-01(12)	(i-4)(100)	Anhydrous succinic acid (1.0)	3.2	52.7	7.9	47.4	6000
Synthetic Example 37	(J-18)	PAA-03(10)	(i-5)(100)	Anhydrous succinic acid (1.1)	5.4	56.8	10.9	53.9	17000
Synthetic Example 38	(J-19)	PAA-05(10)	(i-6)(100)	Butane sultone (2.5)	18.4	48.9	27.5	37.9	12000
Synthetic Example 39	(J-20)	PAA-03(12)	(i-7)(100)	Anhydrous succinic acid (5.1)	15.1	74.7	38.2	48.1	8000
Synthetic Example 40	(J-21)	PAA-08(15)	(i-8)(100)	Anhydrous succinic acid (2.2)	5.9	78.9	16.4	71.5	32000
Synthetic Example 41	(J-22)	PAA-03(14)	(i-9)(100)	Anhydrous cyclohexane carboxylic acid (3.0)	12.5	77.1	21.3	67.8	15000
Synthetic Example 42	(J-23)	PAA-15(15)	(i-10)(100)	Anhydrous succinic acid (2.5)	2.4	28.2	14.6	18.6	18000
Synthetic Example 43	(J-24)	PAA-03(12)	(i-11)(100)	Anhydrous succinic acid (2.1)	8.6	47.5	17.4	36.7	5000
Synthetic Example 44	(J-25)	PAA-05(10)	(i-12)(100)	Acrylic acid (1.2)	10.4	44.7	15.8	38.4	18000
Synthetic Example 45	(J-26)	PAA-05(5)	(i-13)(100)	Anhydrous succinic acid (0.5)	6.9	17.1	9.1	14.3	11000

Table 4

	Resin	Amino group-containing resin (g)	Polyester	X precursor (g)	Acid value of intermediate (mgKOH/g)	Amine value of intermediate (mgKOH/g)	Acid value of target resin (mgKOH/g)	Amine value of target resin (mgKOH/g)	Weight average molecular weight
Synthetic Example 47	(J-28)	SP-012(2)	(i-15)(100)	Vinylphosphonic Acid (0.2)	21.2	23.2	24.6	18.2	15000
Synthetic Example 48	(J-29)	SP-006(2.5)	(i-16)(100)	None	30.5	19.6	30.5	19.6	6000
Synthetic Example 49	(J-30)	SP-012(15)	(i-17)(100)	Anhydrous maleic acid (0.2)	8.6	79.2	10.9	76.2	20000
Synthetic Example 50	(J-31)	SP-006(18)	(i-18)(100)	Anhydrous succinic acid (3.0)	16.2	92.1	27.5	80.2	28000
Synthetic Example 51	(J-32)	SP-006(10)	(i-19)(100)	Anhydrous glutaric acid (2.0)	30.1	30.2	38.2	21.2	35000
Synthetic Example 52	(J-33)	SP-018(3)	(i-15)(100)	None	16.4	27.8	16.4	27.8	8200
Synthetic Example 53	(J-34)	PAA-01(18)	(i-16)(100)	Butane sultone (4.0)	32.4	91.2	21.3	82.6	12000
Synthetic Example 54	(J-35)	PAA-03(15)	(i-17)(100)	Anhydrous succinic acid (3.5)	25.1	75.2	14.6	62.1	24000
Synthetic Example 55	(J-36)	PAA-03(2)	(i-18)(100)	None	17.4	16.2	17.4	16.2	28000
Synthetic Example 56	(J-37)	PAA-05(20)	(i-19)(100)	Acrylic acid (1.5)	9.2	105.4	15.8	98.2	38000

<Example 1>

[Preparation of Titanium Dioxide Liquid Dispersion (Dispersion Composition)]

A mixed liquid having the following composition was subjected to dispersion treatment by using ULTRA APEX MILL manufactured by KOTOBUKI INDUSTRIES Co., Ltd. as a circulation-type dispersion device (bead mill) in the following manner to obtain a titanium dioxide liquid dispersion as a dispersion composition.

-Composition-

· Titanium dioxide (manufactured by ISHIHARA SANGYO KAISHA, LTD. TTO-51(C)) (Purity 75% or more):	150 parts
· Specific resin J-1:	40.5 parts
· Propylene glycol monomethyl ether acetate:	462 parts

The dispersion device is operated under the following conditions.

- Bead diameter: $\phi 0.05$ mm
- Bead Filling Ratio: 75 volume%
- Circumferential Speed: 8 m/sec
- Pump Supply Amount: 10 Kg/hour
- Cooling Water: Tap Water
- Inner volume of bead mill annular passage: 0.15 L
- Amount of mixed liquid for dispersion treatment: 0.44 Kg

After the initiation of dispersion, average particle diameters were measured at a 30 minute interval (time for one pass).

The average particle diameter was decreased with the dispersion time (number of passes), but the variation amounts were gradually decreased. At a time point in which the change in the primary particle diameter when the dispersion time was increased by 30 min became 5 nm or less, the dispersion was terminated. Meanwhile, titanium dioxide particles in the liquid dispersion had a primary particle diameter of 40 nm.

The viscosity at this time was measured to evaluate the dispersibility, and the variation in viscosity after 1 month of dispersion was measured to evaluate the dispersion stability (storage temperature 25°C).

When the viscosity was 15 mPa·s or less, the dispersibility was excellent, and when the viscosity was more than 15 mPa·s, the dispersibility is deteriorated.

The dispersion stability was evaluated in accordance with the following evaluation standard.

The variation in viscosity after 1 month of dispersion is within $\pm 10\%$: A

The variation in viscosity after 1 month of dispersion is more than $\pm 10\%$ and $\pm 20\%$ or less: B

The variation in viscosity after 1 month of dispersion is more than $\pm 20\%$: C

Dispersion compositions corresponding to compositions in Examples 2 to 37 and Comparative Examples 1 and 2 as described below, which had been prepared in accordance with the dispersion composition in Example 1, were also subjected to viscosity measurement to evaluate the dispersibility and the variation in viscosity after 1 month of dispersion was measured to evaluate the dispersion stability (storage temperature 25°C), except that the content of titanium dioxide and the kind of specific resin was changed as in the following Table 5 such that the dispersion compositions correspond to compositions in Examples 2 to 37 and Comparative Examples 1 and 2. The results are shown in Table 5.

Meanwhile, the primary particle diameter of titanium dioxide in the present Example refers to a value obtained by performing measurement on a diluted solution obtained by diluting a mixed solution or a liquid dispersion including titanium dioxide to 80 times with propylene glycol monomethyl ether acetate using a dynamic light scattering method.

This measurement is calculated as a number average particle diameter obtained by performing measurement using MICROTRAC UPA-EX150 manufactured by NIKKISO Co., Ltd.

[Preparation of Curable Composition]

The titanium dioxide liquid dispersion (dispersion composition) obtained above was used and each component was mixed with each other so as to have the following composition, thereby obtaining a curable composition.

—Composition of Curable Composition—

· Titanium dioxide liquid dispersion prepared above (dispersion composition)	78.26 parts
· Dipentaerythritol hexaacrylate	4.36 parts
(Polymerizable compound, following T-1)	
· Oxime-based photopolymerization initiator	0.30 part

(Polymerization initiator, following K-1)

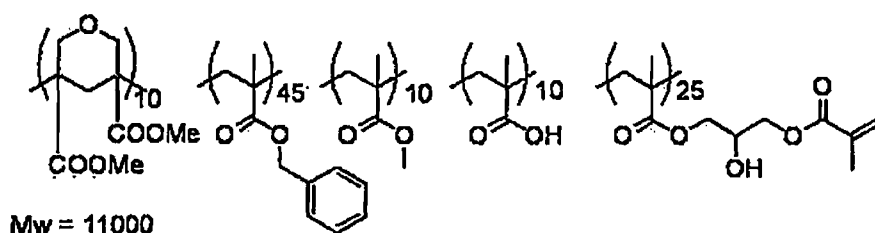
· Binder polymer 2.18 parts

(Following M-1; weight average molecular weight (Mw) and copolymerization ratio (molar ratio) are as follows)

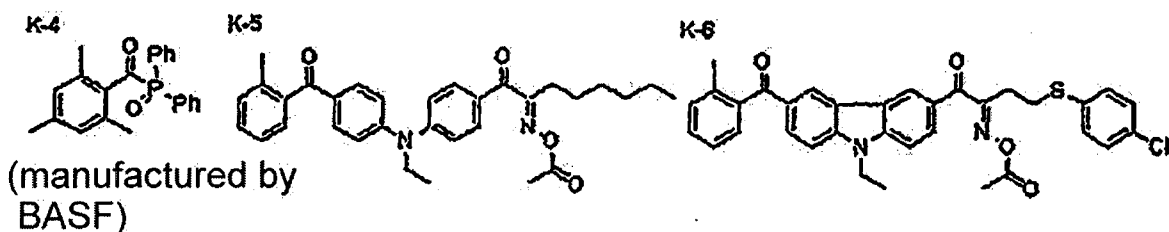
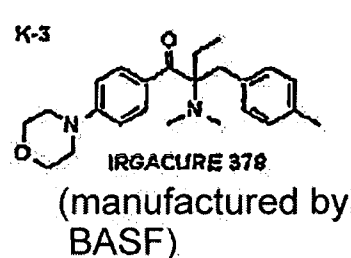
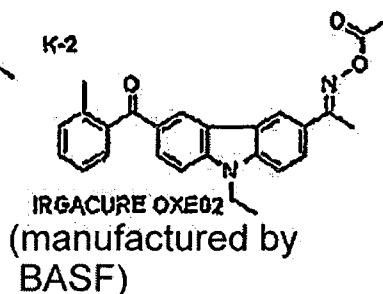
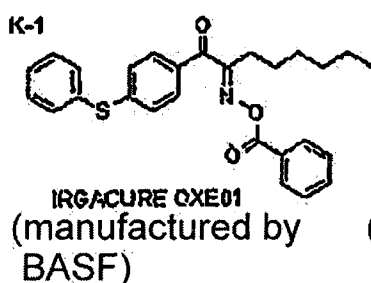
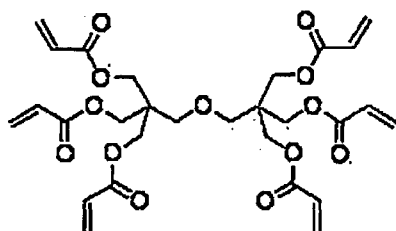
· Surfactant MEGAFAC F-781 0.30 part

· Propylene glycol monomethyl ether acetate 14.60 parts

M-1



T-1



(Manufacture of Transparent Film)

The curable composition obtained above was coated on a 12-inch silicon wafer by a spin coating method, followed by heating at 100°C on a hot plate for 2 min to obtain a coating

film having a film thickness of 1.05 μm . The coating film was heated at 200°C on a hot plate for 5 min to obtain a cured film (film thickness: 1.0 μm) as a transparent film.

[Measurement of Refractive Index of Transparent Film]

For the substrate obtained above, a refractive index of a transparent pattern to light at a wavelength of 500 nm was measured by using ellipsometry manufactured by J.A.Woollam JAPAN Co., Ltd. The light transmittance of the transparent film was measured throughout the wavelength region of from 400 nm to 700 nm by using MCPD Series manufactured by Otsuka Electronics Co., Ltd.

Each of the results is shown in the following Table 5.

[Measurement of Difference in Film Thickness between Central Portion and Peripheral Portion of Wafer]

For a wafer substrate with a transparent film formed thereon, which was obtained above, a difference between a thickness of the transparent film at a center portion of the wafer and a thickness of the transparent film at a portion that was recessed by 3 cm in a direction from a peripheral portion of the wafer to the center portion of the wafer was measured by Dekrak (manufactured by Veeco Instruments Inc.). Numerical results are shown in the following Table 5.

<Examples 2 to 37 and Comparative Examples 1 and 2>

The curable compositions in Examples 2 to 37 and Comparative Examples 1 and 2 were prepared in accordance with Example 1, except that the content of titanium dioxide based on the total solid content of the curable composition and the kinds of specific resin and polymerization initiator were changed as in the following Table 5.

That is, in the example in which the specific resin was changed from the J-1 which was used in Example 1, a titanium dioxide liquid dispersion obtained by using the specific resin shown in Table 5 instead of the J-1 was used in the preparation of the titanium dioxide liquid dispersion used in Example 1.

Meanwhile, in Comparative Examples 1 and 2, Solsperse 5000 manufactured by The Lubrizol Corporation and DISPERBYK180 manufactured by BYK Chemie GmbH were used, respectively, as resins different from the specific resin of the present invention.

In the example in which the polymerization initiator was changed from compound K-1

used in Example 1, a polymerization initiator shown in Table 5 instead of compound K-1 was used in the preparation of the curable composition in Example 1.

The modification of the content (concentration) of titanium dioxide based on the total solid content of the curable composition was performed by supplementing the increased or decreased portion in the content of titanium dioxide with the increase or decrease in the content of a binder polymer, while the total amount of titanium dioxide and the binder based on the total solid content of the curable composition was controlled to the amount as in Example 1.

The curable composition obtained was used to manufacture each of the transparent films in the same manner as in Example 1, followed by evaluation in the same manner as in Example 1. The results are shown in Table 5.

Table 5

	Content of titanium dioxide based on solid content of composition	Resin	Polymerization initiator	Refractive index	Transmittance (%)	Dispersibility (mPa·s)	Dispersion stability	Difference in film thickness of transparent film between center portion and peripheral portion of wafer (nm)
Example 1	60%	J-1	K-1	1.83	98.9	10.9	A	18
Example 2	50%	J-2	K-1	1.75	99.4	9.6	A	16
Example 3	60%	J-3	K-1	1.83	98.5	10.7	A	21
Example 4	40%	J-4	K-1	1.73	99.8	8.9	A	22
Example 5	60%	J-5	K-1	1.83	98.3	10.2	A	17
Example 6	60%	J-6	K-1	1.83	98.5	9.9	A	18
Example 7	60%	J-7	K-1	1.83	98.6	11.2	A	24
Example 8	60%	J-8	K-1	1.83	98.4	10.4	A	22
Example 9	60%	J-9	K-1	1.83	98.2	12.1	A	20
Example 10	60%	J-10	K-2	1.83	99.2	11.4	A	18
Example 11	60%	J-11	K-3	1.83	98.3	10.1	A	26
Example 12	60%	J-12	K-4	1.83	98.7	9.8	A	22
Example 13	60%	J-13	K-1	1.83	99.1	10.5	A	23
Example 14	60%	J-14	K-1	1.83	98.6	12.6	A	30
Example 15	60%	J-15	K-1	1.83	98.4	11.2	A	31
Example 16	60%	J-16	K-1	1.83	98.1	10.5	A	25
Example 17	40%	J-17	K-1	1.75	99.6	7.9	A	29
Example 18	60%	J-18	K-1	1.83	98.4	10.1	A	32
Example 19	60%	J-19	K-1	1.83	98.3	9.6	A	24
Example 20	60%	J-20	K-1	1.83	98.8	11.6	A	31
Example 21	60%	J-21	K-1	1.83	98.7	10.7	A	32
Example 22	60%	J-22	K-5	1.83	98.2	11.2	A	25
Example 23	60%	J-23	K-6	1.83	97.9	10.2	A	29
Example 24	40%	J-24	K-1	1.76	99.7	11.8	A	21
Example 25	60%	J-25	K-1	1.83	99.2	9.7	A	26
Example 26	60%	J-26	K-1	1.83	98.2	10.3	A	30
Example 27	60%	J-27	K-1	1.83	98.6	10.7	A	24

Table 5 (Continued)

	Content of titanium dioxide based on solid content of composition	Resin	Polymerization initiator	Refractive index	Transmittance (%)	Dispersibility (mPa·s)	Dispersion stability	Difference in film thickness of transparent film between center portion and peripheral portion of wafer (nm)
Example 28	60%	J-28	K-1	1.83	99.7	10.5	A	24
Example 29	60%	J-29	K-1	1.83	99.4	9.9	A	21
Example 30	60%	J-30	K-1	1.83	97.6	9.8	A	26
Example 31	60%	J-31	K-1	1.83	97.4	9.9	A	28
Example 32	60%	J-32	K-1	1.83	99.1	10.5	A	32
Example 33	60%	J-33	K-1	1.83	98.8	10.3	A	22
Example 34	60%	J-34	K-1	1.83	97.3	9.6	A	24
Example 35	60%	J-35	K-1	1.83	97.9	9.8	A	25
Example 36	60%	J-36	K-1	1.83	99.7	10.3	A	27
Example 37	60%	J-37	K-1	1.83	97.1	9.2	A	35
Comparative Example 1	60%	Solsperse 5000	K-1	1.71	95.8	21.2	C	82
Comparative Example 2	60%	DISPERBYK180	K-1	1.73	95.2	36.4	C	75

As apparent from Table 5, it can be seen that the dispersion compositions in Comparative Examples 1 and 2, which had not used the specific resin, had high viscosity, the dispersibility was deteriorated, and the dispersion stability was also deteriorated.

Meanwhile, it can be seen that the dispersion composition in Examples 1 to 37, which used the specific resin of the present invention, had low viscosity and thus the dispersibility was excellent and the dispersion stability was also excellent.

It can be seen that the curable composition in Comparative Examples 1 and 2, which did not use the specific resin, had a big difference in film thickness between the center portion and the peripheral portion of the wafer.

Meanwhile, it can be seen that the curable compositions in Examples 1 to 37, which used the specific resin of the present invention, had a small difference in film thickness between the center portion and the peripheral portion of the wafer.

It can be seen that the transparent films formed by using the curable compositions in Comparative Examples 1 and 2, which did not use the specific resin, had low transmittance and refractive index.

Meanwhile, it can be seen that the transparent films formed by using the curable compositions in Examples 1 to 37, which used the specific resin of the present invention, had high transmittance and refractive index.

Although examples in which a transparent film is formed on a silicon wafer have been described in the above Examples, in the case of manufacturing a solid-state image sensing device, the silicon wafer may be changed only into a substrate for a solid-state image sensing device, with a photodiode, a light-shielding film, a device protective film, and the like formed thereon.

A light-shielding film formed of tungsten, in which only a light-receiving part of a photodiode is open, is formed on a silicon wafer with the photodiode and a transfer electrode formed thereon, and a device protective layer formed of silicon nitride is formed such that the entire surface of the light-shielding film formed and the photodiode light-receiving part (opening part in the light-shielding film) are covered.

Subsequently, on the device protective layer formed, each of red pixels, blue pixels, and green pixels with a side length of 1.4 μm was formed by a method described in Example 16 of the official gazette of Japanese Patent Application Laid-Open No. 2010-210702 A and then a color filter was prepared.

Thereon, the curable composition in the Example, controlled as described above, was coated so as to have a film thickness of 1.5 μm , heated at 100°C for 2 min by using a hot plate, followed by heating at 200°C for 5 min by using a hot plate to cure the film.

HPR-204ESZ-9-5 mPa·s (resist liquid manufactured by FUJIFILM Electronic Materials Co., Ltd.) was coated thereon, followed by heating at 90°C for 1 min by using a hot plate. The coating film was exposed at 100 mJ/cm^2 via a mask having a plurality of square patterns with a side length of 1.4 μm by an i-ray stepper (product name: FPA-3000i5+, manufactured by Canon Inc.). Here, the mask was disposed such that the plurality of square patterns in the mask had positions corresponding to red pixels, blue pixels and green pixels in the color filter, respectively.

The film was subjected to puddle development using the alkaline developing solution HPRD-429E (manufactured by FUJIFILM Electronic Materials Co., Ltd.) at room temperature for 60 sec, followed by rinsing with pure water by spin shower for 20 sec. Thereafter, the film was further washed with pure water, and then the substrate was dried with a high-speed rotation to form a resist pattern. The film was subjected to a post-bake treatment on a hot plate at 200°C for 300 sec to shape the resist into a lens-type shape.

The substrate thus-obtained was subjected to a dry etching treatment under the following conditions by using a dry etching device (U-621: manufactured by Hitachi High-Technologies Corporation) and then a transparent film of the present invention having a high refractive index was processed so as to be used as a microlens.

- RF Power: 800 W
- Antenna bias: 100 W
- Wafer bias: 500 W
- Chamber inner pressure: 0.5 Pa
- Substrate temperature: 50°C
- Mixed gas species and flow rate: $\text{CF}_4/\text{C}_4\text{F}_6/\text{O}_2/\text{Ar}=175/25/50/200$ ml/min
- Photoresist etching rate: 140 nm/min

When the device obtained was used to photograph an image, a good image may be obtained.

Industrial Applicability

According to the present invention, it is possible to provide a dispersion composition having excellent dispersibility and dispersion stability, and having a high refractive index and

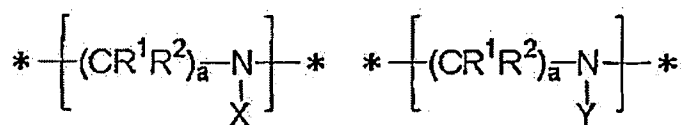
light transmittance when prepared as a curable composition, which is able to form a film having a small difference in film thickness between the center portion and the peripheral portion thereof even when the composition is applied on a large size wafer, and a curable composition, a transparent film, a microlens and a solid-state image sensing device using the same, a method for manufacturing a transparent film, a method for manufacturing a microlens and a method for manufacturing a solid-state image sensing device.

This application is based on Japanese patent application Nos. JP 2011-111735 filed on May 18, 2011, JP 2012-113719 filed on May 17, 2012, the entire contents of which are hereby incorporated by reference, the same as if set forth at length.

CLAIMS

1. A dispersion composition, comprising:
colorless or transparent metal oxide particles (A) having a primary particle diameter of from 1 nm to 100 nm;
a resin (B1) which has a repeating unit having a group X having a functional group with a pKa of 14 or less, and has an oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000 in a side chain thereof, and which also contains a basic nitrogen atom; and
a solvent (C).
2. The dispersion composition according to claim 1, wherein the resin (B1) is a resin (B2) which has a repeating unit containing a nitrogen atom bonded to the group X having a functional group with a pKa of 14 or less, and an oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000 in a side chain thereof.
3. The dispersion composition according to claim 1 or 2, wherein the dispersion composition comprises:
colorless or transparent metal oxide particles (A) having a primary particle diameter of from 1 nm to 100 nm,
a resin (B) having (i) at least one repeating unit containing a nitrogen atom, selected from a poly(lower alkyleneimine)-based repeating unit, a polyallylamine-based repeating unit, a polydiallylamine-based repeating unit, a metaxylenediamine-epichlorohydrin polycondensate-based repeating unit and a polyvinylamine-based repeating unit, wherein the repeating unit has a group X that has a functional group with a pKa of 14 or less and the group X is bonded to the nitrogen atom, and (ii) an oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000 in the side chain thereof, and
a solvent (C).
4. The dispersion composition according to any one of claims 1 to 3, wherein the functional group with a pKa of 14 or less which the group X has is carboxylic acid, sulfonic acid or -COCH₂CO-.

5. The dispersion composition according to claim 3 or 4, wherein the resin (B) is a resin comprising a repeating unit represented by the following general formula (I-1) and a repeating unit represented by the general formula (I-2):

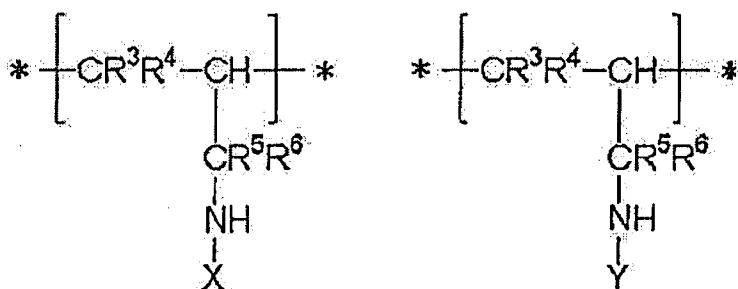


Formula(I-1)

Formula(I-2)

in the general formula (I-1) and the general formula (I-2),
 each of R^1 and R^2 independently represents a hydrogen atom, a halogen atom or an alkyl group,
 each of a 's independently represents an integer of from 1 to 5,
 * represents a linking portion between the repeating units,
 X represents a group having a functional group having a pKa of 14 or less,
 Y represents an oligomer chain or polymer chain having the number of atoms of from 40 to 10,000.

6. The dispersion composition according to claim 3 or 4, wherein the resin (B) is a resin containing a repeating unit represented by the following general formula (II-1) and a repeating unit represented by the general formula (II-2):



Formula(II-1)

Formula(II-2)

in the general formula (II-1) and the general formula (II-2),
 each of R^3 , R^4 , R^5 and R^6 independently represents a hydrogen atom, a halogen atom or an alkyl group,
 * represents a linking portion between the repeating units,
 X represents a group having a functional group having a pKa of 14 or less,
 Y represents an oligomer chain or polymer chain having the number of atoms of from

40 to 10,000.

7. The dispersion composition according to any one of claims 1 to 6, wherein the oligomer chain or polymer chain Y having the number of atoms of from 40 to 10,000 has a structure represented by the following formula (III-1):



Formula(III-1)

in the general formula (III-1), Z is a polymer or oligomer having a polyester chain as a partial structure, and represents a residue except the carboxyl group from a polyester having a free carboxylic acid represented by the following general formula (IV):



Formula(IV)

in the general formula (IV), Z is the same as Z in the general formula (III-1).

8. A curable composition, comprising:
the dispersion composition according to any one of claims 1 to 7,
wherein the dispersion composition further contains a polymerizable compound (D)
and a polymerization initiator (E).

9. The curable composition according to claim 8, further comprising:
a binder polymer.

10. The curable composition according to claim 8 or 9,
wherein the polymerization initiator (E) is an oxime-based polymerization initiator.

11. The curable composition according to any one of claims 8 to 10, which is used
for forming a microlens.

12. A transparent film, which is formed by using the curable composition
according to any one of claims 8 to 11.

13. A microlens, which is formed by using the transparent film according to claim 12.
14. A solid-state image sensing device comprising:
the microlens according to claim 13.
15. A method for manufacturing a transparent film, comprising:
a process of applying the curable composition according to any one of claims 8 to 10 on a wafer,
a subsequent first heating process of heating the composition, and
a subsequent second heating process of heating the composition at a temperature higher than the temperature in the first heating process.
16. A method for manufacturing a microlens, comprising:
a process of subjecting the transparent film according to claim 12 to post bake treatment to shape the transparent film, and
a process of dry etching the transparent film.
17. A method for manufacturing a solid-state image sensing device, comprising:
a process of forming red pixels, blue pixels, and green pixels on a substrate for a solid-state image sensing device having at least a photodiode, a light-shielding film, and a device protective film,
a process of applying the curable composition according to any one of claims 8 to 10 and performing heating,
a process of forming a resist pattern,
a process of shaping the formed resist pattern into a lens-type shape by performing post-bake treatment, and
a process of performing dry etching.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/063402

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. See extra sheet

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. C08L33/04-33/26, 39/00-39/02, 79/00-79/02, 101/02-101/08, C08F2/44-2/50, C08J3/09, C08K3/22, G02B1/04, G03F7/004, G03F7/031, H01L27/14

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

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2009-203462 A (FUJI FILM CO LTD) 2009.09.10, Claims, [0001], [0018]-[0326] & WO 2009/096452 A1 & EP 2246385 A1 & US 2011/3241 A1	1-10, 12 11-17
Y A	JP 2007-99943 A (JSR CORP) 2007.04.19, [0002]-[0003] & WO 2007/043449 A1	11-17 1-10
P, X P, A	JP 2011-127096 A (FUJI FILM CO LTD) 2011.06.30, Claims, [0018]-[0310] & WO 2011/062198 A1	1-2, 4, 7-17 3, 5-6
A	JP 2010-6932 A (FUJI FILM CO LTD) 2010.01.14, Claims (Family:none)	1-17

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

* Special categories of cited documents:

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

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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

"&" document member of the same patent family

Date of the actual completion of the international search

13.08.2012

Date of mailing of the international search report

28.08.2012

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/063402

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2007-16208 A (CANON FINETECH INC) 2007.01.25, Claims & US 2006/281847 A1	1-17
A	JP 2008-40477 A (FUJIFILMELECTRONIC MATERIALS CO LTD) 2008.02.21, Claims & CN 101105546 A & KR 2008-6452 A	1-17
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/063402

CLASSIFICATION OF SUBJECT MATTER

C08L101/02 (2006.01) i, C08F2/44 (2006.01) i, C08F2/48 (2006.01) i,
C08J3/09 (2006.01) i, C08K3/22 (2006.01) i, G02B1/04 (2006.01) i,
G03F7/004 (2006.01) i, G03F7/031 (2006.01) i, H01L27/14 (2006.01) i