

DESCRIPTION

TITLE OF THE INVENTION

5 Photosensitive Resin Composition and Method for
Producing Same

TECHNICAL FIELD

[0001]

10 The present invention relates to a photosensitive
resin composition useful as an electrical component in
semiconductor devices, microplastic lenses, liquid
crystal polarizing plates, optical waveguides and the
like which are intended mainly for optical applications,
and a resin insulating film used for an
15 electrical/electronic material of semiconductor devices,
multilayer circuit boards and the like. More
specifically, the present invention relates to a material
for camera module plastic mini-lenses or camera module
peripherals of cellular phones, monitor cameras and the
20 like; a material for the formation of a microplastic lens
for optical communication, a microplastic lens for solid
imaging devices such as CCD or CMOS image sensor, an LED
encapsulant, a photonic crystal for achieving high LED
luminance, a thin-film transistor array in the display
25 field, or a material for the antireflection film, a
material for optical elements for a polarizing plate in a
liquid crystal projector, and a material for the
formation of a buffer coat or an interlayer insulating
film of an LSI chip.

30

BACKGROUND ART

[0002]

35 A plastic lens is easy to mold and inexpensive
compared to glass, and therefore is widely used in a
variety of optical products. As the material therefor,
various transparent materials, for example, a
thermoplastic plastic, such as polymethyl methacrylate or

polystyrene; and a thermosetting plastic, such as polydiethylene glycol bis(allyl carbonate), are used. However, as indicated in Patent Documents 1 and 2, most conventional materials merely have heat resistance of 200°C or less even when improved, and do not ensure resistance to a solder reflow heat at 260°C.

[0003]

In general, a siloxane polymer having a ≡Si-O-Si≡ structure has high heat resistance. Patent Document 3 discloses a polysiloxane having a molecular weight of 3,000 to 10,000, which is obtained by polymerizing a silanediol and an alkoxysilane by a two-stage process.

RELATED ART

PATENT DOCUMENT

[0004]

Patent Document 1: Japanese Unexamined Patent Publication (Kokai) No. 09-31136

Patent Document 2: Kokai No. 2004-245867

Patent Document 3: International Publication No. 2008/123224, pamphlet

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005]

An object of the present invention is to provide a photosensitive resin composition having excellent characteristics, such as thermal shock resistance high enough to cause no cracking or peeling even when passed through a cold-heat cycle of -40°C to 125°C after curing, which is useful for production of products with integrated electronic parts or of solid-state imaging elements that requires a reflow soldering process, a resin usable for the composition, and a cured product using the composition.

MEANS TO SOLVE THE PROBLEMS

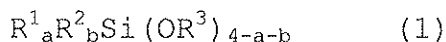
[0006]

The present inventors have studied how to improve a siloxane-containing photosensitive resin so as to attain the above-described object, as a result, it has been found that, when only a specific silanol compound is condensation-polymerized and is added with a photopolymerization initiator, or when a specific silanol compound and a specific alkoxysilane compound are mixed and condensation-polymerized and a photopolymerization initiator is added thereto, a photosensitive resin excellent in the thermal shock resistance can be obtained. The present inventors have also invented a method for increasing the molecular weight of a polysiloxane. The present invention has been accomplished based on these findings, i.e., the present invention is as follows.

[0007]

- [1] A photosensitive resin composition comprising:
- (a) 100 parts by mass of a polyorganosiloxane having a polymerizable functional group; and
- (b) from 0.01 to 30 parts by mass of a photopolymerization initiator;

wherein the polyorganosiloxane is obtained by means of a method of mixing at least one alkoxysilane compound represented by following general formula (1):

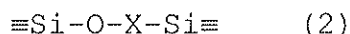


{wherein R^1 is an ester bond-containing organic group having a carbon number of 2 to 17, and at least one R^1 has an acryloyl group or a methacryloyl group; R^2 is, when a plurality of R^2 s are present, each is independently, an aliphatic group having a carbon number of 1 to 10, which may have a substituent; R^3 is, when a plurality of R^3 s are present, each is independently, a methyl group or an ethyl group; a is an integer of 1 or 2; b is an integer of 0, 1 or 2; and a+b is 3 or less}

and a catalyst to obtain a mixture, and polymerizing the

mixture,

wherein the polyorganosiloxane contains a structure represented by following general formula (2):

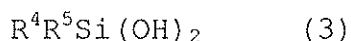


5 {wherein X is an organic group having a carbon number of 1 to 15}, and

wherein from 5 to 60% by number of Si atoms in the polyorganosiloxane are contained in the structure represented by general formula (2).

10 **[0008]**

[2] The photosensitive resin composition according to [1], wherein the polyorganosiloxane is obtained by means of a method of mixing the at least one alkoxysilane compound represented by general formula (1), at least one
15 silanol compound represented by following general formula (3):



{wherein each of R^4 and R^5 is an aliphatic, alicyclic or aromatic group having a carbon number of 3
20 to 10, which may have a substituent} and a catalyst to obtain a mixture, and polymerizing the mixture.

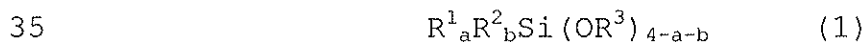
[0009]

[3] The photosensitive resin composition according to [1] or [2], wherein from 10 to 40% by number of Si
25 atoms in the polyorganosiloxane are contained in the structure represented by general formula (2).

[0010]

[4] A photosensitive resin composition comprising:
30 (a) 100 parts by mass of a polyorganosiloxane; and
 (b) from 0.01 to 30 parts by mass of a photopolymerization initiator;

wherein the polyorganosiloxane is obtained by means of a method of mixing at least one alkoxysilane compound represented by following general formula (1):



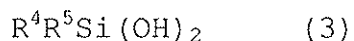
{wherein R^1 is an ester bond-containing organic group having a carbon number of 2 to 17, and at

least one R¹ has an acryloyl group or a methacryloyl group; R² is, when a plurality of R²s are present, each is independently, an aliphatic group having a carbon number of 1 to 10, which may have a substituent; R³ is, when a plurality of R³s are present, each is independently, hydrogen, a methyl group or an ethyl group; a is an integer of 1 or 2; b is an integer of 0, 1 or 2; and a+b is 3 or less} and a catalyst to obtain a mixture, and polymerizing the mixture, and

wherein the ratio of the peak area derived from a carboxylic acid of the ester bond and the peak area derived from an alcohol of the ester bond in the polyorganosiloxane by ¹H-NMR spectrum is decreased by 5 to 60% compared to the mixture of the alkoxysilane compound before polymerization.

[0011]

[5] The photosensitive resin composition according to [4], wherein the polyorganosiloxane is obtained by means of a method of mixing the at least one alkoxysilane compound represented by general formula (1), at least one silanol compound represented by following general formula (3):



{wherein each of R⁴ and R⁵ is an aliphatic, alicyclic or aromatic group having a carbon number of 3 to 10, which may have a substituent} and a catalyst to obtain a mixture, and polymerizing the mixture.

[0012]

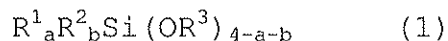
[6] The photosensitive resin composition according to [4] or [5], wherein the ratio of the peak area derived from a carboxylic acid of the ester bond and the peak area derived from an alcohol of the ester bond in the ¹H-NMR spectrum of the polyorganosiloxane is decreased by 10 to 40% compared to the mixture of the alkoxysilane compound and the silanol compound before polymerization.

[0013]

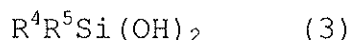
[7] A photosensitive resin composition comprising:

(a) 100 parts by mass of a polyorganosiloxane; and
(b) from 0.01 to 30 parts by mass of a
photopolymerization initiator;

5 wherein the polyorganosiloxane is obtained by means
of a method of mixing at least one alkoxysilane compound
represented by following general formula (1):



10 {wherein R^1 is an ester bond-containing
organic group having a carbon number of 2 to 17, and at
least one R^1 has an acryloyl group or a methacryloyl
group; R^2 is, when a plurality of R^2 s are present, each is
independently, an aliphatic group having a carbon number
of 1 to 10, which may have a substituent; R^3 is, when a
plurality of R^3 s are present, each is independently, a
15 methyl group or an ethyl group; a is an integer of 1 or
2; b is an integer of 0, 1 or 2; and $a+b$ is 3 or less},
at least one silanol compound represented by following
general formula (3):

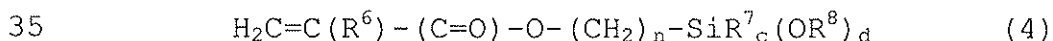


20 {wherein each of R^4 and R^5 is an aliphatic,
alicyclic or aromatic group having a carbon number of 3
to 10, which may have a substituent} and a catalyst to
obtain a mixture, and polymerizing the mixture, and

wherein an area having a weight average molecular
25 weight of 1,050 or more in terms of standard polystyrene
as measured by gel permeation chromatography (GPC) is 70%
or more of the whole GPC peak area.

[0014]

30 [8] The photosensitive resin composition according
to any one of [1] to [7], wherein the alkoxysilane
compound represented by general formula (1) is at least
one alkoxysilane compound represented by following
general formula (4):



{wherein R^6 is hydrogen or a methyl group; R^7 is,
when a plurality of R^7 s are present, each is

independently, an aliphatic group having a carbon number of 1 to 10, which may have a substituent; R^8 is, when a plurality of R^8 s are present, each is independently, a methyl group or an ethyl group; c is an integer of 0, 1 or 2; d is an integer of 1, 2 or 3; c+d is 3 or less; and n is from 1 to 14).

[0015]

[9] The photosensitive resin composition according to any one of [2], [3] and [5] to [8], wherein at least one of R^4 and R^5 in general formula (3) is an alicyclic group having a carbon number of 3 to 10, which may have a substituent.

[0016]

[10] The photosensitive resin composition according to any one of [1] to [9], further comprising (c) from 0.1 to 1,000 parts by mass of an ethylenically unsaturated addition-polymerizable monomer per 100 parts by mass of the polyorganosiloxane.

[0017]

[11] The photosensitive resin composition according to [10], wherein the ethylenically unsaturated addition-polymerizable monomer is a compound containing an alicyclic group.

[0018]

[12] The photosensitive resin composition according to any one of [1] to [11], further comprising at least one additive selected from the group consisting of an ultraviolet absorber, a light stabilizer, an adhesion aid, a polymerization inhibitor, a sensitizer, an antioxidant and a smoothness-imparting agent.

[0019]

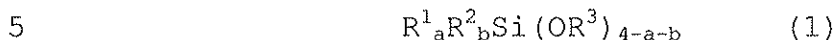
[13] The photosensitive resin composition according to any one of [1] to [12], wherein the concentration of the alkali metal or alkaline earth metal in the photosensitive resin composition is from 0.1 to 500 ppm.

[0020]

[14] A production process of a polyorganosiloxane,

comprising the following steps of:

i) producing (a) a polyorganosiloxane by mixing at least one alkoxysilane compound represented by following general formula (1):



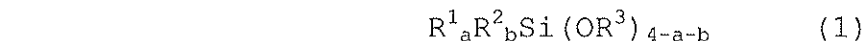
{wherein R^1 is an ester bond-containing organic group having a carbon number of 2 to 17, and at least one R^1 has an acryloyl group or a methacryloyl group; R^2 is, when a plurality of R^2 s are present, each is
10 independently, an aliphatic group having a carbon number of 1 to 10, which may have a substituent; R^3 is, when a plurality of R^3 s are present, each is independently, a methyl group or an ethyl group; a is an integer of 1 or 2; b is an integer of 0, 1 or 2; and a+b is 3 or less},
15 from 0.01 to 0.5 equivalents of water per one equivalent of OR^3 contained in the alkoxysilane compound present in the reaction system, and a catalyst to obtain a mixture, and reacting the mixture at 20 to 130°C for 0.1 to 20 hours while removing an alcohol produced by the reaction
20 from the reaction system; and

ii) washing the polyorganosiloxane with a solvent incapable of dissolving the polyorganosiloxane.

[0021]

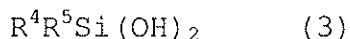
[15] A production process of a polyorganosiloxane,
25 comprising the following steps of:

i) producing (a) a polyorganosiloxane by mixing at least one alkoxysilane compound represented by following general formula (1):



{wherein R^1 is an ester bond-containing organic group having a carbon number of 2 to 17, and at least one R^1 has an acryloyl group or a methacryloyl group; R^2 is, when a plurality of R^2 s are present, each is
independently, an aliphatic group having a carbon number
35 of 1 to 10, which may have a substituent; R^3 is, when a plurality of R^3 s are present, each is independently, a methyl group or an ethyl group; a is an integer of 1 or

2; b is an integer of 0, 1 or 2; and a+b is 3 or less},
at least one silanol compound represented by following
general formula (3):



5 {wherein each of R^4 and R^5 is an aliphatic,
alicyclic or aromatic group having a carbon number of 3
to 10, which may have a substituent} and a catalyst to
obtain a mixture, and reacting the mixture at 20 to 130°C
for 0.1 to 20 hours while removing an alcohol produced by
10 the reaction from the reaction system; and

ii) washing the polyorganosiloxane with a solvent
incapable of dissolving the polyorganosiloxane.

[0022]

[16] The production process according to [14] or
15 [15], wherein the catalyst is at least one compound
selected from the group consisting of an alkali metal
hydroxide and an alkaline earth metal hydroxide.

[0023]

[17] The production process according to any one of
20 [14] to [16], wherein the catalyst is $Ba(OH)_2$ and/or a
hydrate thereof.

[0024]

[18] The production process according to any one of
[14] to [17], wherein the amount of the catalyst is from
25 0.05 to 30 mol% based on a total number of moles of
silicon (Si).

[0025]

[19] The production process according to any one of
[14] to [18], wherein the amount of the catalyst is from
30 0.1 to 10 mol% based on a total number of moles of
silicon (Si).

[0026]

[20] The production process according to any one of
[14] to [19], wherein the solvent is an alcohol or an
35 acetonitrile.

[0027]

[21] A cured product obtained by photocuring the

photosensitive resin composition according to any one of [1] to [13], or a photosensitive resin composition comprising (a) a polyorganosiloxane obtained by the production process according to any one of [14] to [20] and (b) a photopolymerization initiator.

[0028]

[22] A method for producing a molded article, comprising the following steps of:

filling a shape-forming mold with the photosensitive resin composition according to any one of [1] to [13], or a photosensitive resin composition comprising (a) a polyorganosiloxane obtained by the production process according to any one of [14] to [20] and (b) a photopolymerization initiator,

pressing the opening of the mold against a substrate or another mold,

exposing the photosensitive resin composition to light from the mold and/or substrate side to obtain a photocured product,

separating the mold from the substrate, or separating the molds from both surfaces of the photocured product, and

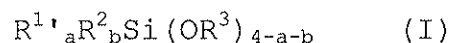
heating only the photocured product, or the photocured product with the substrate.

[0029]

[23] A molded article obtained by the method according to [22].

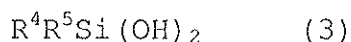
[0030]

[24] A polyorganosiloxane obtained by means of a method of mixing at least one alkoxysilane compound represented by following general formula (I):



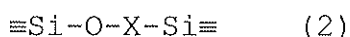
{wherein R^1 is an ester bond-containing organic group having a carbon number of 2 to 17; R^2 is, when a plurality of R^2 s are present, each is independently, an aliphatic group having a carbon number of 1 to 10, which may have a substituent; R^3 is, when a

plurality of R³s are present, each is independently, a methyl group or an ethyl group; a is an integer of 1 or 2; b is an integer of 0, 1 or 2; and a+b is 3 or less}, at least one silanol compound represented by following general formula (3):



{wherein each of R⁴ and R⁵ is an aliphatic, alicyclic or aromatic group having a carbon number of 3 to 10, which may have a substituent} and a catalyst to obtain a mixture, and polymerizing the mixture,

wherein the polyorganosiloxane contains a structure represented by following general formula (2):



{wherein X is an organic group having a carbon number of 1 to 15}, and

wherein from 5 to 60% by number of Si atoms in the polyorganosiloxane are contained in the structure represented by general formula (2).

[0031]

[25] The polyorganosiloxane according to [24], wherein R^{1'} in general formula (I) is a group having an acrylic acid ester and/or a methacrylic acid ester.

EFFECTS OF THE INVENTION

[0032]

According to the present invention, a resin or photosensitive resin composition, having excellent characteristics, such as thermal shock resistance high enough to cause no cracking or peeling even when passed through a cold-heat cycle, and being useful for the production of products with integrated electronic parts or of solid-state imaging elements that requires a reflow soldering process.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033]

[Fig. 1] Fig. 1 shows a ¹H-NMR spectrum chart of the

polyorganosiloxane in an embodiment of the present invention.

5 [Fig. 2] Fig. 2 shows a GPC chart of the polyorganosiloxane in an embodiment of the present invention.

[Fig. 3] Fig. 3 shows a ^{13}C -NMR spectrum chart of the polyorganosiloxane in an embodiment of the present invention.

10 [Fig. 4] Fig. 4 shows a ^1H -NMR spectrum chart of the polyorganosiloxane in another embodiment of the present invention.

[Fig. 5] Fig. 5 shows a ^1H -NMR spectrum chart of the polyorganosiloxane in still another embodiment of the present invention.

15 [Fig. 6] Fig. 6 shows a GPC chart of the polyorganosiloxane in still another embodiment of the present invention.

[Fig. 7] Fig. 7 shows an HH COSY spectrum of the polyorganosiloxane in an embodiment of the present invention.

[Fig. 8] Fig. 8 shows a CH COSY spectrum of the polyorganosiloxane in an embodiment of the present invention.

25 MODE FOR CARRYING OUT THE INVENTION

[0034]

<Photosensitive Resin Composition>

The photosensitive resin composition of the present invention comprises:

30 (a) a polyorganosiloxane which is obtained by means of a method of mixing a specific alkoxysilane compound and a catalyst to obtain a mixture, and polymerizing the mixture, and which contains a structure represented by following general formula (2):

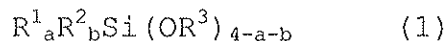


{wherein X is an organic group having a carbon number of 1 to 15}; and

(b) a photopolymerization initiator.

[0035]

The alkoxysilane compound is at least one alkoxysilane compound represented by following general formula (1):



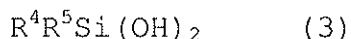
{wherein R^1 is an ester bond-containing organic group having a carbon number of 2 to 17, and at least one R^1 has an acryloyl group or a methacryloyl group; R^2 is, when a plurality of R^2 s are present, each is independently, an aliphatic, alicyclic or aromatic group having a carbon number of 1 to 10, which may have a substituent; R^3 is, when a plurality of R^3 s are present, each is independently, a methyl group or an ethyl group; a is an integer of 1 or 2; b is an integer of 0, 1 or 2; and a+b is 3 or less}.

[0036]

In view of storage stability, it is preferable to use, as the polyorganosiloxane (a), a polyorganosiloxane obtained by means of a method of mixing at least one alkoxysilane compound represented by above general formula (1), a specific silanol compound and a catalyst to obtain a mixture, and polymerizing the mixture.

[0037]

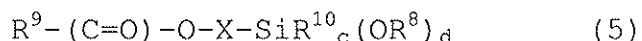
In this case, the silanol compound is at least one silanol compound represented by following general formula (3):



{wherein each of R^4 and R^5 is an aliphatic, alicyclic or aromatic group having a carbon number of 3 to 10, which may have a substituent}.

[0038]

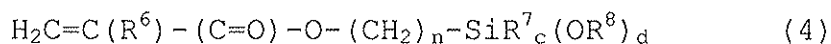
The alkoxysilane represented by above general formula (1) is preferably at least one alkoxysilane compound represented by following formula (5):



{wherein R^9 is an aliphatic, alicyclic or

aromatic group having a carbon number of 1 to 15, which may have a substituent, and at least one R⁹ has an acrylic acid ester and/or a methacrylic acid ester; X is an aliphatic, alicyclic or aromatic group having a carbon number of 1 to 15, which may have a substituent; R¹⁰ is, when a plurality of R¹⁰s are present, each is independently, an aliphatic group having a carbon number of 1 to 10, which may have a substituent; R⁸ is, when a plurality of R⁸s are present, each is independently, a methyl group or an ethyl group; c is an integer of 0, 1 or 2; d is an integer of 1, 2 or 3; c+d is 3 or less; and n is from 1 to 14}, more preferably a compound having an acrylic acid ester and/or a methacrylic acid ester.

Among others, it is preferable in view of UV photosensitivity to use at least one alkoxysilane compound represented by following formula (4):



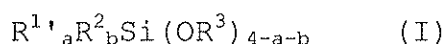
{wherein R⁶ is hydrogen or a methyl group; R⁷ is, when a plurality of R⁷s are present, each is independently, an aliphatic, alicyclic or aromatic group having a carbon number of 1 to 10, which may have a substituent; R⁸ is, when a plurality of R⁸s are present, each is independently, a methyl group or an ethyl group; c is an integer of 0, 1 or 2; d is an integer of 1, 2 or 3; c+d is 3 or less; and n is from 1 to 14}.

Examples of the alkoxysilane compound represented by above general formula (4) include 3-methacryloxypropyltrimethoxysilane, 3-methacryloxypropyltriethoxysilane, 3-methacryloxypropylmethyldimethoxysilane, 3-acryloxypropyltrimethoxysilane, 3-acryloxypropyltriethoxysilane, 2-methacryloxyethyltrimethoxysilane, 2-methacryloxyethyltriethoxysilane, 2-macryloxyethylmethyldimethoxysilane, 2-acryloxyethyltrimethoxysilane, 2-acryloxyethyltriethoxysilane,

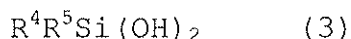
methacryloxymethyltrimethoxysilane,
methacryloxymethyltriethoxysilane,
methacryloxymethylmethyldimethoxysilane,
acryloxymethyltrimethoxysilane,

5 acryloxymethyltriethoxysilane and the like. An ester
bond-containing alkoxysilane without a polymerizable
functional group, such as 3-
acetoxypopyltrimethoxysilane, may be also used.

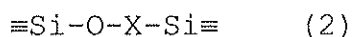
In the case of obtaining a polyorganosiloxane which
10 is produced by means of a method of mixing at least one
alkoxysilane compound represented by following general
formula (I):



{wherein R^1 is an ester bond-containing
15 organic group having a carbon number of 2 to 17; R^2 is,
when a plurality of R^2 s are present, each is
independently, an aliphatic group having a carbon number
of 1 to 10, which may have a substituent; R^3 is, when a
plurality of R^3 s are present, each is independently, a
20 methyl group or an ethyl group; a is an integer of 1 or
2; b is an integer of 0, 1 or 2; and a+b is 3 or less},
at least one silanol compound represented by following
general formula (3):



25 {wherein each of R^4 and R^5 is an aliphatic,
alicyclic or aromatic group having a carbon number of 3
to 10, which may have a substituent} and a catalyst to
obtain a mixture, and polymerizing the mixture, and which
contains a structure represented by following general
30 formula (2):



{wherein X is an organic group having a
carbon number of 1 to 15}, and which contains from 5 to
60% by number of Si atoms in the structure represented by
35 above general formula (2), only an ester bond-containing
alkoxysilane not having a polymerizable functional group,
such as 3-acetoxypopyltrimethoxysilane, may be used as

the at least one alkoxysilane compound represented by above general formula (I), other than the above-described alkoxysilane compound.

5 By using the above-described polyorganosiloxane, a resin excellent in thermal shock resistance can be obtained.

[0039]

10 As the catalyst, a compound that accelerates hydrolysis of an alkoxy group of the alkoxysilane compound and a condensation reaction between silanols produced by the hydrolysis or between an alkoxysilane and a silanol and also advances an ester hydrolysis reaction or a transesterification reaction during polymerization, can be used.

15 **[0040]**

As the catalyst used in the reaction of the alkoxysilane compound and the silanol compound, a compound that accelerates a dealcoholization condensation reaction of a silanol group of the silanol compound with an alkoxy group of the alkoxysilane compound and also advances an ester hydrolysis reaction or a transesterification reaction during polymerization, can be used.

[0041]

25 The catalyst may be either an acidic compound or a basic compound, and includes, for example, a metal alkoxide, an inorganic acid, an organic acid, an inorganic base, an organic base, and a phosphazene compound. Among others, an alkali metal hydroxide, an alkaline earth metal oxide, an ammonium compound or the like is preferred, and specific examples thereof include Ba(OH)₂, Ca(OH)₂, Mg(OH)₂, KOH, LiOH, NH₃, NH₄OH, NR₄(OH), NR₄Cl, NR₄Br, NR₄I and the like. In NR₄(OH), NR₄Cl, NR₄Br and NR₄I, R is an aliphatic, alicyclic or aromatic group
30 having a carbon number of 1 to 10, which may have a substituent. The catalyst is more preferably an alkali metal hydroxide, an alkaline earth metal hydroxide or the

like, still more preferably an alkaline earth metal hydroxide, and specific examples thereof include $\text{Ba}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, etc. Hydrates of $\text{Ba}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ may be also used, and in view of stability, and a reaction with good reproducibility because the reaction time can be shortened and the reaction time in an inhomogeneous state becomes short, it is more preferable to use $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$.

[0042]

The amount of the catalyst added is preferably a concentration that allows for appropriate progress of a hydrolysis reaction by a hydrate water or the like contained in the catalyst or transesterification reaction or the like, and the amount of the catalyst is, for example, from 0.05 to 30 mol%, and in view of transparency and reaction controllability, preferably from 0.1 to 20 mol%, still more preferably from 0.1 to 10 mol%, yet still more preferably from 0.2 to 10 mol%, based on the number of moles of Si atom charged. The number of moles of Si atom charged is a number of moles of Si atom calculated by adding up the alkoxysilane compound represented by above general formula (1), the silanol compound represented by above general formula (3) and other condensable silane compounds present in the reaction system, and the "mol%" expressing the catalyst amount indicates how many moles the catalyst is added based on the number of moles of Si atom.

[0043]

In the silanol compound represented by above general formula (3), in view of stability of the compound, R^4 and R^5 is preferably an aromatic or alicyclic group which is a bulky substituent. In view of light resistance and heat resistance, a compound where at least one of R^4 and R^5 is an alicyclic group having a carbon number of 3 to 10, which may have a substituent, is more preferred as the silanol compound. In addition, in view of excellent transparency, dicyclohexylsilanediol or

dicyclopentylsilanediol is still more preferred as the silanol compound.

[0044]

5 With respect to a mixing ratio of the alkoxysilane compound represented by above general formula (1) and the silanol compound represented by above general formula (3), the ratio of the alkoxysilane compound represented by above general formula (1) to 100 mol of the silanol compound represented by above general formula (3) is from 10 to 200 mol, preferably from 20 to 180 mol, more preferably from 30 to 150 mol, still more preferably from 40 to 120 mol, and in view of molecular weight and UV photosensitivity of a resin to be obtained, most preferably from 60 to 100 mol.

15 **[0045]**

In the case where the alkoxysilane compound represented by above general formula (1) and the silanol compound represented by above general formula (3) are mixed, and reacted in the presence of a catalyst, the reaction temperature is from 20 to 130°C, preferably from 30 to 100°C, more preferably from 40 to 80°C, and the reaction time is from 0.1 to 20 hours, preferably from 0.2 to 10 hours, still more preferably from 0.3 to 5 hours. The atmosphere in the reaction vessel may be a nitrogen atmosphere or an air atmosphere. Water may or may not be positively added to the reaction system. Even in the case of not positively adding water to the reaction system, water in the hydrate compound of the catalyst or water in the silanol may be present in the reaction system. In the case of using only the alkoxysilane compound represented by above general formula (1), a minimum amount of water may be used, and the amount is preferably from 0.001 to 0.5 equivalents per one equivalent of an alkoxy group bonded to the Si atom of the alkoxysilane compound.

35 **[0046]**

For the purpose of, for example, decreasing the

coefficient of thermal expansion of the cured product or adjusting the refractive index of the cure product, a fine particle of silica, zirconia, titania or the like may be added to the reaction system.

5 **[0047]**

<Reaction of Alkoxysilane Compound or Reaction between Alkoxysilane Compound and Silanol Compound>

10 The alkoxysilane compound represented by above general formula (1) and water, or the alkoxysilane compound represented by above general formula (1) and the silanol compound represented by above general formula (3) are mixed and reacted in the presence of a catalyst. The ^1H -NMR spectrum measurement of the reaction mixture is performed every certain time (for example, 15 minutes, 30 minutes, 60 minutes), and the reaction is allowed to proceed while confirming the decrease ratio of the peak area on the side derived from a carboxylic acid of the ester bond contained in the alkoxysilane compound represented by above general formula (1). For example, 20 in the case of an ester bond " A-C(=O)-O-B ", A is the side derived from a carboxylic acid of the ester bond, and B is the side derived from an alcohol of the ester bond. Due to hydrolysis or solvolysis of the ester, the peak area of a certain proton derived from A in ^1H -NMR 25 decreases, and the decrease ratio of the peak area on the side derived from a carboxylic acid indicates how much the peak area of a certain proton derived from A is decreased based on another certain proton that undergoes no change during reaction.

30 **[0048]**

 The decrease ratio is determined by comparison with NMR spectrum of a raw material. For example, in the case of using $\text{H}_2\text{C}=\text{C}(\text{Me})-(\text{C}=\text{O})-\text{O}-(\text{CH}_2)_3-\text{Si}(\text{OMe})_3$ as the raw material, at the beginning of charging it to a reaction vessel, i.e., in the NMR spectrum of the raw material, a 35 proton of $\equiv\text{Si}-\underline{\text{CH}_2}-$ appears near 0.6 ppm, a peak of a proton of $\underline{\text{H}_2\text{C}}=\text{C}<$ appears near 5.5 ppm and near 6.0 ppm,

the peak areas thereof is 2:2 and the ratio thereof is 1.

On the other hand, an ester bond is formed by
condensing a carboxylic acid and an alcohol, and in a
polyorganosiloxane wherein the carboxylic acid moiety of
the ester bond decreased, the peak area of $\text{H}_2\text{C}=\text{C}<$
corresponding to the carboxylic acid moiety of the ester
bond is decreased compared to the peak area of $\equiv\text{Si}-\text{CH}_2-$
corresponding to the alcohol moiety of the ester bond,
and the ratio of the peak area of $\text{H}_2\text{C}=\text{C}<$ to the peak area
of $\equiv\text{Si}-\text{CH}_2-$ becomes 1 or less, whereby the percentage by
which the carboxylic acid moiety of the ester bond
decreased can be calculated.

As a specific example, when a polyorganosiloxane as
shown in Fig. 1 is obtained, the sum of peak areas of two
 $\text{H}_2\text{C}=\text{C}<$ is 1.997, the peak area of $\equiv\text{Si}-\text{CH}_2-$ is 2.885 and in
turn, the peak area ratio is $1.997/2.885$, i.e., 0.69,
revealing 31% reduction of the peak area derived from a
carboxylic acid of the ester bond, in other words, the
decrease in the carboxylic acid moiety of the ester bond
by 31%, compared to the ratio at the beginning of
charging the raw material to a reaction vessel, i.e., the
peak area ratio of 1 of the raw material. In this case,
the ^1H -NMR spectrum is based on the peak of CHCl_3 taken at
7.24 ppm.

[0049]

The decrease in the peak area derived from a
carboxylic acid of the ester bond of the alkoxysilane
compound represented by above general formula (1) can be
controlled by changing, for example, the catalyst amount,
the time, the temperature, the pressure in the reaction
vessel or the like. For example, the decreasing rate can
be increased by changing the conditions, such as an
increase in the catalyst amount, elongation of time, rise
in temperature or the like.

As a specific example, in the case of using an
alkoxysilane having a methacrylic acid ester as the

alkoxysilane represented by above general formula (1) and using $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ as the catalyst, when the catalyst is used in a usually-needed concentration of 0.1 mol% based on the total Si amount, the peak area derived from a carboxylic acid of the ester bond is not decreased even by setting the reaction temperature at 50°C and the reaction time to 2 hours. However, when the reaction is carried out by increasing the catalyst amount to 0.3 mol%, an organosiloxane that the peak area derived from a carboxylic acid of the ester bond is decreased by about 30% can be synthesized. In this way, the peak area derived from a carboxylic acid of the ester bond can be decreased by a desired quantity by changing the catalyst amount, the temperature or the reaction time.

[0050]

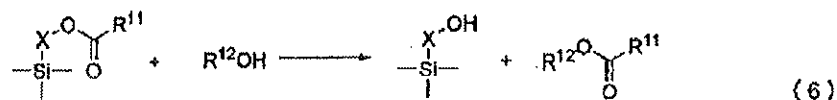
A percentage by which the ester bond in the alkoxysilane compound represented by above general formula (1) decreases during the polymerization reaction is from 5 to 60%, preferably from 7 to 50%, more preferably from 10 to 40%, and most preferably from 15 to 35%, based on the amount of the alkoxysilane compound represented by above general formula (1) which is charged into an reaction system. The decrease in the percentage corresponds to the percentage by which the peak area derived from a carboxylic acid of the ester bond of the alkoxysilane compound represented by above general formula (1) decreases.

[0051]

The decrease in the peak area of the carboxylic acid moiety of the ester bond is considered to occur because due to, for example, the production of an alcohol (methanol or ethanol) by condensation of an alkoxy moiety of the alkoxysilane compound represented by above general formula (1) with a silanol moiety of the silanol represented by above general formula (3) as well as a slight amount of water and the presence of a basic catalyst, a hydrolysis reaction, a transesterification

reaction and the like of the ester bond proceeds, as shown by following reaction formula (6):

[Chem. 1]

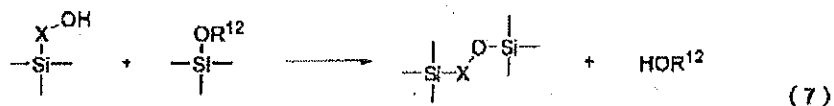


5 (wherein X is an organic group having a carbon number of 1 to 15, R¹¹ is an organic group having a carbon number of 0 to 15, the sum of carbon numbers of X and R¹¹ is from 1 to 16, and R¹² is a methyl group, an ethyl group or hydrogen).

10 [0052]

By the hydrolysis reaction and transesterification reaction of the ester bond, the moiety derived from a carboxylic acid disappears, and the moiety derived from an alcohol remains. Furthermore, it is believed that due to an alcohol exchange reaction or the like of the produced alcohol with an alkoxy group of the alkoxy silane compound represented by above general formula (1) and a silanol group of the silanol compound represented by above general formula (3), a crosslinking reaction represented by following formula (7) takes place:

20 [Chem. 2]



(wherein X is an organic group having a carbon number of 1 to 15, preferably an organic group having a carbon number of 2 to 10, more preferably an organic group having a carbon number of 3 to 5 and in view of heat resistance and crack resistance, most preferably an organic group having a carbon number of 3, and R¹² is a methyl group, an ethyl group or hydrogen).

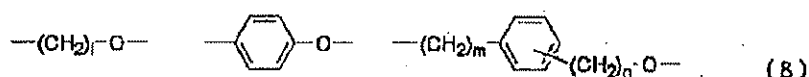
30 [0053]

In other words, it is considered that a polyorganosiloxane (a) where the alkylene alcohol or phenylene alcohol produced resulting from disappearance of the ester moiety is partially or entirely crosslinked with an alkoxysilane compound represented by general formula (1), a silanol compound represented by general formula (3) or a polycondensation product of at least one kind of such a compound, is obtained.

[0054]

The crosslinking reaction enables increasing the molecular weight. In turn, the polyorganosiloxane (a) having the structure represented by above general formula (2) can be obtained. By having the structure of above general formula (2), an effect that the thermal shock resistance is excellent is provided. In above general formula (2), X may have an aromatic group in the main chain thereof, and is preferably an alkyl group or an aromatic group, which may be further substituted. Specifically, -X-O- includes structures represented by following general formula (8):

[Chem. 3]



(wherein l is from 1 to 15, m is from 0 to 9, n is from 0 to 9, and n+m<9). In view of light resistance, an alkyl group is preferred as X, and in view of heat resistance, the carbon number of X is preferably from 2 to 10, more preferably from 3 to 5, and most preferably 3.

[0055]

It can also be confirmed, for example, by ¹H-NMR and ¹³C-NMR spectrum measurements that the polyorganosiloxane has the structure represented by above general formula (2).

[0056]

Specifically, in the case of using H₂C=C(CH₃)-(C=O)-

O-(CH₂)₃-Si(OCH₃)₃ as the alkoxysilane compound represented by above general formula (1), the structure represented by above general formula (2) becomes $\equiv\text{Si}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}\equiv$, and in the ¹H-NMR spectrum, the peak of the underlined proton of the H₂C=C(CH₃)-(C=O)-O-CH₂-CH₂-CH₂-Si≡ structure which keeps from disappearance of the ester bond appears at 3.9-4.2 ppm, whereas the peak of the underlined proton of the $\equiv\text{Si}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}\equiv$ structure appears near 3.4-3.9 ppm. Furthermore, in the ¹³C-NMR spectrum, the peak of the underlined carbon of the H₂C=C(CH₃)-(C=O)-O-CH₂-CH₂-CH₂-Si≡ structure appears near 66.5 ppm, whereas the peak of the underlined carbon of the HO-CH₂-CH₂-CH₂-Si≡ structure produced by above reaction formula (6) appears near 62.0 ppm and the peak of the underlined carbon of the $\equiv\text{Si}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}\equiv$ structure produced by above reaction formula (7) appears near 64.5 ppm (here, the peak of CHCl₃ is set at 7.24 ppm in the ¹H-NMR spectrum, the peak in the center of CDCl₃ is set at 77.0 ppm in the ¹³C-NMR spectrum, and the ¹³C-NMR spectrum is measurement in NNE mode; see Figs. 1 and 3).

[0057]

These peaks can be identified by two-dimensional measurement of NMR spectrum. Fig. 7 is an HH COSY spectrum, and Fig. 8 is a CH COSY spectrum. In general, the HH COSY spectrum allows a correlation to appear in the peaks of hydrogen atoms bonded respectively to two carbon atoms in an adjacent relationship, and the CH COSY spectrum allows a correlation to appear in the peaks of a carbon atom and a hydrogen atom which are bonded.

In the HH COSY spectrum shown in Fig. 7, it is seen that the peak at 3.4-3.9 ppm and the peak near 1.0 ppm have a relationship, and the peak near 1.0 ppm and the peak near 0.0 ppm have a relationship. It is also seen from the CH COSY spectrum shown in Fig. 8 that the peak at 64.5 ppm in ¹³C-NMR spectrum has a relationship with the peak at 3.4-3.9 ppm in ¹H-NMR spectrum. By

comprehensively evaluating these results, respective peaks can be identified (here, when the peak in ^1H NMR spectrum has its basis on the highest magnetic field side, the peak in COSY spectrum is corrected to 0 ppm, and the spectrum in COSY is completely shifted about 0.6 ppm to the high magnetic field side compared to the actual ^1H NMR spectrum).

[0058]

The abundance ratio of the structure represented by above general formula (2) can be calculated by the above identifications. specifically, assuming that the ^{13}C NMR spectrum shown in Fig. 3 is obtained in the case of using $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-(\text{C}=\text{O})-\text{O}-(\text{CH}_2)_3-\text{Si}(\text{OCH}_3)_3$ as the alkoxysilane compound represented by above general formula (1), the peak area of the underlined carbon of the $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-(\text{C}=\text{O})-\text{O}-\underline{\text{CH}_2}-\text{CH}_2-\text{CH}_2-\text{Si}\equiv$ structure is 0.853, the peak area of the underlined carbon of the $\text{HO}-\underline{\text{CH}_2}-\text{CH}_2-\text{CH}_2-\text{Si}\equiv$ structure is 0.099, and the peak area of the underlined carbon of the $\equiv\text{Si}-\text{O}-\underline{\text{CH}_2}-\text{CH}_2-\text{CH}_2-\text{Si}\equiv$ structure is 0.415. In this connection, when the alkoxysilane compound represented by above general formula (1) and the silanol compound represented by above general formula (3) are charged at 50:50, the $\equiv\text{Si}-\text{O}-\underline{\text{CH}_2}-\text{CH}_2-\text{CH}_2-\text{Si}\equiv$ structure is calculated as that 30% by number of Si atoms contained in the polymer form the bond in the structure represented by above general formula (2).

[0059]

In addition, even when the charging ratio of the alkoxysilane compound or silanol compound is not known, the Si atom content can be measured by a ^{29}Si NMR spectrum using an internal standard, the ester structure content can be measured by a ^1H NMR spectrum using an internal standard, the structures can be identified by a ^{13}C NMR spectrum (NNE mode), an HH COSY spectrum and a CH COSY spectrum, and the content percentage of $\equiv\text{Si}-\text{O}-\text{X}-\text{Si}\equiv$ can be calculated based on the identified structures.

[0060]

The NMR spectrum was measured by using JNM-GSX400. The ^1H NMR spectrum was measured at 400 MHz, and the ^{13}C NMR spectrum was measured at 100 MHz.

5 **[0061]**

In view of crack resistance, easy handleability and photocurability, out of Si atoms contained in the polyorganosiloxane, the percentage of the number of Si atoms forming the bond in the structure represented by
10 above general formula (2) is from 5 to 60%, preferably from 7 to 50%, more preferably from 10 to 40%, and most preferably from 15 to 35%.

[0062]

As the method for increasing the molecular weight
15 while maintaining the equivalent of the crosslinking functional group of the polyorganosiloxane, a method of adding a boron compound or a method of adding a phosphorus compound and a peroxide may be also used.

[0063]

20 Low molecular materials (for example, dimer, trimer and tetramer) may be also removed by washing the polyorganosiloxane obtained in the reaction step with a solvent incapable of dissolving the polyorganosiloxane. The solvent incapable of dissolving the
25 polyorganosiloxane in the washing step includes, for example, water, an alcohol (such as methanol or ethanol), an acetonitrile, etc.

[0064]

In the washing step, a solvent incapable of
30 dissolving a polyorganosiloxane is added to the polyorganosiloxane obtained in the reaction step, or the polyorganosiloxane obtained in the reaction step is added to a solvent incapable of dissolving the polyorganosiloxane, and is then stirred. Stirring a
35 mixture of the polyorganosiloxane and the solvent is continued in inhomogeneous state and thereafter, the mixture is left standing still. After the mixture is

separated into a polyorganosiloxane layer and a solvent layer, the polyorganosiloxane layer is collected or the solvent layer is removed, whereby washing can be performed.

5 **[0065]**

The residual catalyst can be reduced by means of the washing step. In view of storage stability of the polyorganosiloxane resin and the resin composition, the amount of the residual catalyst in the resin composition is preferably from 0.1 to 500 ppm.

10 **[0066]**

<Increase of Molecular Weight of Polyorganosiloxane>

The polyorganosiloxane (a) for use in the photosensitive resin composition of the present invention is obtained by means of a method of mixing the alkoxysilane compound represented by above general formula (1), the silanol compound represented by above general formula (3) and the catalyst to obtain a mixture, and polymerizing the mixture, wherein in the polyorganosiloxane, the area having a weight average molecular weight of 1,050 or more in terms of standard polystyrene as measured by gel permeation chromatography (GPC) is 70% or more of the whole GPC peak area.

20 **[0067]**

The method for evaluating the molecular weight (GPC measurement) is as follows.

A calibration curve is prepared by using HLC-8020 manufactured by Tosoh Corporation with a differential refractometer (RI) as the detector and series-connected G5000HHR, G4000HHR, G3000HHR and G2500HHR manufactured by Tosoh Corporation as columns and using a polystyrene (TSK Standards produced by Tosoh Corporation, molecular weight: 1,090,000; 706,000; 355,000; 190,000; 96,400; 37,900; 18,100; 9,100; 5,970; 2,630; 1,056; and 500) as the standard polystyrene under the condition of 40°C, and measurement is performed using THF as the solvent at a flow rate of 1 mL/min.

[0068]

The silanol compound, the alkoxysilane compound, the catalyst, the reaction conditions and the like are the same as those described above.

5 **[0069]**

Increase of the molecular weight is achieved by forming the structure represented by above general formula (2). Accordingly, the molecular weight may be controlled by controlling the structure represented by
10 above general formula (2), i.e., the reactions represented by above reaction formulae (6) and (7).

[0070]

These reactions can be controlled by changing the reaction temperature, the reaction time, the reaction
15 pressure, the catalyst amount, and the catalyst type.

[0071]

<Production Process of Polyorganosiloxane>

The production process of (a) a polyorganosiloxane, comprises, in order:

20 i) a step of producing a polyorganosiloxane by mixing the at least one alkoxysilane compound represented by above general formula (1) and a catalyst to obtain a mixture, and reacting the mixture at a temperature of 20 to 130°C, preferably from 30 to 100°C, more preferably
25 from 40 to 80°C, for a reaction time of 0.1 to 20 hours, preferably from 0.2 to 10 hours, more preferably from 0.3 to 5 hours, while removing an alcohol produced by the reaction from the reaction system; and

30 ii) a step of washing the polyorganosiloxane with a solvent incapable of dissolving the polyorganosiloxane.

[0072]

Water may be added to the reaction system, but the amount of water added is preferably from 0.01 to 0.5 equivalents, more preferably from 0.05 to 0.45
35 equivalents, and in view of storage stability and reactivity due to the terminal alkoxy structure, still more preferably from 0.1 to 0.4 equivalents, per one

equivalent of an alkoxy group bonded to the Si atom contained in the alkoxysilane compound present in the reaction system.

[0073]

5 The production process of (a) a polyorganosiloxane, comprises, in order:

 i) a step of producing a polyorganosiloxane by mixing the at least one alkoxysilane compound represented by above general formula (1), the at least one silanol
10 compound represented by above general formula (3) and a catalyst to obtain a mixture, and reacting the mixture at a temperature of 20 to 130°C, preferably from 30 to 100°C, more preferably from 40 to 80°C, for a reaction time of 0.1 to 20 hours, preferably from 0.2 to 10 hours, more
15 preferably from 0.3 to 5 hours, while removing an alcohol produced by the reaction from the reaction system; and

 ii) a step of washing the polyorganosiloxane with a solvent incapable of dissolving the polyorganosiloxane.

[0074]

20 In the production process of the polyorganosiloxane (a), removal of the alcohol in the production step i) is preferably performed by reducing the pressure at a temperature of 30 to 80°C. That is, the production process of the polyorganosiloxane is characterized by
25 performing the reaction while removing the produced alcohol to the outside of the reaction system under atmospheric pressure when the reaction temperature is not less than the boiling point of the produced alcohol, or under reduced pressure when the reaction temperature is
30 not more than the boiling point. Due to this removal, the amount of an alcohol in a reaction vessel is reduced, and high controllability of reaction results (i.e., breakage of an ester is retarded and thereby can be easily controlled).

35 **[0075]**

 As the catalyst used for polymerization, a compound

that accelerates a dealcoholization condensation reaction of a silanol group of the silanol compound with an alkoxy group of the alkoxy silane compound, and advances an ester hydrolysis reaction or a transesterification reaction during polymerization, can be used. The catalyst may be either an acidic compound or a basic compound, and includes, for example, a metal alkoxide, an inorganic acid, an organic acid, an inorganic base, an organic base, and a phosphazene compound, etc. Among others, an alkali metal hydroxide, an alkaline earth metal hydroxide, an ammonium compound or the like is preferred, and specific examples thereof include $\text{Ba}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, KOH , LiOH , NH_3 , NH_4OH , $\text{NR}_4(\text{OH})$, NR_4Cl , NR_4Br , NR_4I , etc. In $\text{NR}_4(\text{OH})$, NR_4Cl , NR_4Br and NR_4I , R is an aliphatic, alicyclic or aromatic group having a carbon number of 1 to 10, which may have a substituent. The catalyst is more preferably an alkali metal hydroxide, an alkaline earth metal hydroxide or the like, still more preferably an alkaline earth metal hydroxide, and specific examples thereof include $\text{Ba}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, etc. Hydrates of $\text{Ba}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ may be also used, and in view of stability and reaction with good reproducibility because the reaction time, specifically the reaction time in an inhomogeneous state can be shortened, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ is more preferably used.

[0076]

The amount of the catalyst added is preferably a concentration that allows for progression of a hydrolysis reaction by a hydrate water or the like contained in the catalyst or transesterification reaction or the like, and the concentration is, for example, from 0.05 to 30 mol%, and in view of transparency and reaction controllability, preferably from 0.1 to 20 mol%, still more preferably from 0.1 to 10 mol%, yet still more preferably from 0.2 to 10 mol%, based on the number of moles of Si atom which is charged to a reaction system. The number of moles of Si atom charged is a number of moles of Si atom

calculated by adding up the alkoxysilane compound represented by above general formula (1), the silanol compound represented by above general formula (3) and other condensable silane compounds present in the reaction system, and the mol% expressing the catalyst amount indicates how many moles the catalyst is added based on the number of moles of Si atom.

[0077]

In the case where the catalyst is precipitated during reaction or during drying, only the obtained polyorganosiloxane (a) is preferably dissolved with a solvent capable of dissolving the polyorganosiloxane and incapable of dissolving the catalyst, for example, when the catalyst is an alkali metal hydroxide or an alkaline earth metal hydroxide, such as $\text{Ba}(\text{OH})_2$, with cyclohexane, toluene or the like, and then filtered, whereby the catalyst can be removed. In this case, the solvent added is gradually removed and then dried under reduced pressure and heating. The temperature at the drying is from 50 to 130°C, preferably from 80 to 130°C, the pressure is 20 hPa or less, preferably 15 hPa or less, and the drying time is 10 minutes or more, preferably 30 minutes or more, more preferably 1 hour.

[0078]

By washing the resulting polyorganosiloxane (a) with a solvent incapable of dissolving the polyorganosiloxane, low-molecular materials may be reduced. As the solvent, for example, methanol, ethanol, acetonitrile, dimethylsulfoxide, water or the like can be used, as described above, depending on the molecular weight of the produced polyorganosiloxane (a).

[0079]

The solubility of the low-molecular material differs depending on the solvent used and therefore, with respect to the number of washings, the washing can be performed a plurality of times until the low-molecular material is removed in a desired amount.

[0080]

With respect to the specific washing method, as described above, the solvent is added to the polyorganosiloxane (a), or the polyorganosiloxane (a) is added to the solvent, to obtain a mixture, and the mixture is stirred, thereby dissolving the low molecular material in the solvent, and after stirring for a necessary time, the mixture is left standing still to cause separation into a polyorganosiloxane layer and a solvent layer. Thereafter, the solvent layer is removed or the polyorganosiloxane layer is collected, whereby a polyorganosiloxane in which the amount of the low-molecular material is reduced can be isolated.

[0081]

The polyorganosiloxane (a) after isolation is subjected to removal of the solvent and then dried under reduced pressure and heating condition, whereby a polyorganosiloxane in which the amount of the low-molecular material is reduced is obtained.

[0082]

<Photopolymerization Initiator Contained in Photosensitive Resin Composition>

Preferred compounds as the photopolymerization initiator (b) for use in the photosensitive resin composition of the present invention include the followings:

- (1) a benzophenone derivative: for example, benzophenone, methyl o-benzoylbenzoate, 4-benzoyl-4'-methyl diphenyl ketone, dibenzyl ketone and fluorenone;
- (2) an acetophenone derivative: for example, 2,2'-diethoxyacetophenone, 2-hydroxy-2-methylpropiophenone, 2,2-dimethoxy-1,2-diphenylethan-1-one (IRGACURE(registered trademark) 651, produced by BASF), 1-hydroxycyclohexyl phenyl ketone (IRGACURE(registered trademark) 184, produced by BASF), 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one (IRGACURE(registered trademark) 907, produced by BASF),

2-hydroxy-1-{4-[4-(2-hydroxy-2-methylpropionyl)-benzyl]-phenyl}-2-methylpropan-1-one (IRGACURE(registered trademark) 127, produced by BASF) and methyl phenylglyoxylate;

5 (3) a thioxanthone derivative: for example, thioxanthone, 2-methylthioxanthone, 2-isopropylthioxanthone and diethylthioxanthone;

(4) a benzyl derivative: for example, benzyl, benzyl dimethyl ketal and benzyl- β -methoxyethyl acetal;

10 **[0083]**

(5) a benzoin derivative: for example, benzoin, benzoin methyl ether and 2-hydroxy-2-methyl-1-phenylpropan-1-one (DAROCURE(registered trademark) 1173, produced by BASF);

15 (6) an oxime-based compound: for example, 1-phenyl-1,2-butanedione-2-(O-methoxycarbonyl)oxime, 1-phenyl-1,2-propanedione-2-(O-methoxycarbonyl)oxime, 1-phenyl-1,2-propanedione-2-(O-ethoxycarbonyl)oxime, 1-phenyl-1,2-propanedione-2-(O-benzoyl)oxime, 1,3-diphenylpropanetrione-2-(O-ethoxycarbonyl)oxime, 1-phenyl-3-ethoxypropanetrione-2-(O-benzoyl)oxime, 1,2-octanedione, 1-[4-(phenylthio)-2-(O-benzoyloxime)] (IRGACURE(registered trademark) OXE-01, produced by BASF), and ethanone, 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-, 1-(O-acetyloxime) (IRGACURE(registered trademark) OXE02 produced by BASF);

20
25

(7) an α -hydroxy ketone-based compound: for example, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propan-1-one and 2-hydroxy-1-{4-[4-(2-hydroxy-2-methylpropionyl)-benzyl]phenyl}-2-methylpropane;

30

[0084]

(8) an α -aminoalkylphenone-based compound: for example, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (IRGACURE(registered trademark) 369 produced by BASF) and 2-dimethylamino-2-(4-methylbenzyl)-1-(4-

35

morpholin-4-yl-phenyl)butan-1-one (IRGACURE(registered trademark) 379 produced by BASF);

(9) a phosphine oxide-based compound: for example, bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide
5 (IRGACURE(registered trademark) 819 produced by BASF), bis(2,6-dimethoxybenzoyl)-2,4,4-trimethyl-pentylphosphine oxide and 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide (Lucirin (registered trademark), TPO, produced by BASF); and

10 (10) a titanocene compound: for example, bis(η^5 -2,4-cyclopentadien-1-yl)-bis(2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl)titanium (IRGACURE(registered trademark) 784 produced by BASF).

In using the above photopolymerization initiators
15 (b), one compound may be used alone, or a mixture of two or more thereof may be used.

[0085]

Among the above photopolymerization initiators (b), in view of photosensitivity and transparency, a benzoin derivative (5) and a phosphine oxide-based compound (9)
20 are preferred. The amount of the photopolymerization initiator (b) added is from 0.01 to 30 parts by mass, preferably from 0.1 to 5 parts by mass, more preferably from 0.2 to 2 parts by mass, still more preferably from
25 0.3 to 1 part by mass, per 100 parts by mass of the polyorganosiloxane (a). The amount of the photopolymerization initiator (b) added is 0.01 parts by mass or more from the standpoint of obtaining a practical cured pattern, and 30 parts by mass or less in view of
30 transparency.

[0086]

<Ethylenically Unsaturated Addition-Polymerizable Monomer Contained in Photosensitive Resin Composition>

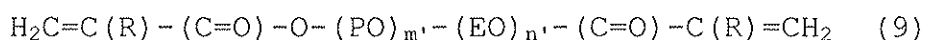
The photosensitive resin composition of the present
35 invention preferably further contains (c) an ethylenically unsaturated addition-polymerizable monomer (hereinafter, sometimes referred to as "monomer"). As

the monomer added to the photosensitive resin composition, from the standpoint of enhancing the crack resistance, heat resistance and hardness, a compound containing an acryloyl group or a methacryloyl group can be used.

[0087]

Specific examples of the monomer which can be used are described below.

The monomer for enhancing the crack resistance includes a monomer having a polyalkylether chain or an oligoalkylether chain, as represented by following general formula (9):



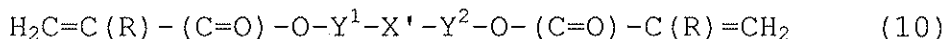
{wherein R is hydrogen or a methyl group, PO is a propylene oxide group, EO is an ethylene oxide group, m' is a number of less than 30, n' is a number of less than 30, and when both PO and EO are present, PO and EO may exist in a random or block manner and m'+n' is a number of less than 60}.

[0088]

The monomer includes, for example, a polyethylene glycol diacrylate [number of ethylene glycol units: from 2 to 20], a polyethylene glycol dimethacrylate [number of ethylene glycol units: from 2 to 20], a poly(1,2-propylene glycol)diacrylate [number of 1,2-propylene glycol units: from 2 to 20], and a poly(1,2-propylene glycol)dimethacrylate [number of 1,2-propylene glycol units: from 2 to 20].

[0089]

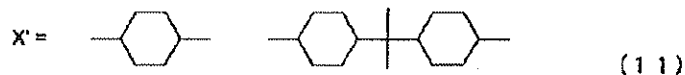
The monomer for enhancing the heat resistance is preferably a compound having an alicyclic group, and includes, for example, an alicyclic group-containing monomer, as represented by following general formula (10):



{wherein R is hydrogen or a methyl group, each of Y¹ and Y² is an organic group having a carbon number of 1 to

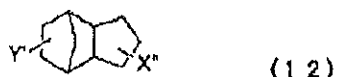
90 and containing an ethylene oxide group and/or a propylene oxide group, and X' is a cyclohexyl group-containing substituent, as represented by following formula (11):

5 [Chem. 4]



and a polycyclic structure-containing monomer, as represented by following general formula (12):

[Chem. 5]



10

{wherein each of Y' and X'' is hydrogen or an organic group containing an alkyl group, an ethylene oxide group or a propylene oxide group, and at least one of Y' and X'' is an acryloyloxy group, a methacryloyloxy group, an acryloyloxymethyl group or a methacryloyloxymethyl group}.

15

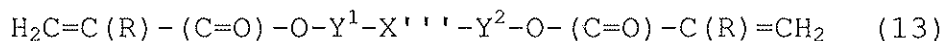
[0090]

The monomers represented by above general formulae (10) and (12) include, for example, 1,4-cyclohexane diacrylate, 1,4-cyclohexane dimethacrylate, an ethoxylated (hydrogenated bisphenol A) diacrylate [number of ethylene glycol units: from 2 to 30], an ethoxylated (hydrogenated bisphenol A) dimethacrylate [number of ethylene glycol units: from 2 to 30], tricyclodecanedimethanol dimethacrylate, tricyclodecanedimethanol diacrylate, dicyclopentanyl acrylate, dicyclopentenyl oxyethyl acrylate, dicyclopentenyl acrylate, dicyclopentanyl methacrylate, dicyclopentenyl oxyethyl methacrylate, etc.

30

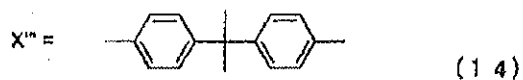
[0091]

The monomer for rising the refractive index includes a benzene ring-containing monomer, as represented by following general formula (13):



5 {wherein R is hydrogen or a methyl group, each of Y¹ and Y² is an organic group having a carbon number of 1 to 90 and containing an ethylene oxide group and/or a propylene oxide group, and X''' is an aromatic group-containing substituent, as represented by following
10 formula (14):

[Chem. 6]



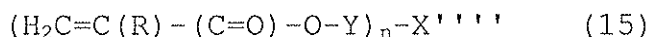
}).

[0092]

The monomer represented by above general formula
15 (13) includes, for example, a bisphenol A diglycidyl ether-acrylic acid adduct, a bisphenol A diglycidyl ether-methacrylic acid adduct, an ethoxylated bisphenol A diacrylate [number of ethylene glycol units: from 2 to 30], and an ethoxylated bisphenol A dimethacrylate
20 [number of ethylene glycol units: from 2 to 30].

[0093]

The monomer for enhancing the hardness and
photosensitivity includes a monomer having three or more
acryloyl or methacryloyl groups, as represented by
25 following general formula (15):



{wherein R is hydrogen or a methyl group, Y is an
organic group having a carbon number of 1 to 90 and
containing an ethylene oxide group and/or a propylene
oxide group, X'''' is an n-valent organic group having a
30 carbon number of 1 to 6, and n is 3 or 4}.

[0094]

The monomer represented by above general formula

(15) includes, for example, a pentaerythritol acrylate, a pentaerythritol tetraacrylate, a trimethylolpropane triacrylate, an ethoxylated trimethylolpropane triacrylate [number of ethylene glycol units: from 2 to 20], a trimethylolpropane trimethacrylate, a tri-2-hydroxyethylisocyanurate triacrylate, a tri-2-hydroxyethylisocyanurate trimethacrylate, ditrimethylolpropane triacrylate, ditrimethylolpropane tetraacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, etc. In addition, in using these monomers, if desired, one monomer may be used alone, or two or more thereof may be mixed and used.

[0095]

In view of crack resistance, heat resistance, refractive index and viscosity (handleability), it is preferable to use an alicyclic group-containing monomer. Specific examples of the alicyclic group-containing monomer include a tricyclodecanedimethanol dimethacrylate, a tricyclodecanedimethanol diacrylate, a dicyclopentanyloxy acrylate, a dicyclopentanyloxy methacrylate, hydrogenated bisphenol ethylene oxide-modified acrylate (number of ethylene oxide units: 10), a hydrogenated bisphenol ethylene oxide-modified methacrylate (number of ethylene oxide units: 10), etc.

[0096]

In view of higher crack resistance, it is more preferable to further use an alkyleneoxy group-containing monomer in combination with the alicyclic group-containing monomer. Specific examples of the alkyleneoxy group-containing monomer include a polyethylene glycol #400 acrylate ($m'=0$, $n'=9$), a polyethylene glycol #600 acrylate ($m'=0$, $n'=14$), a polyethylene glycol #400 methacrylate ($m'=0$, $n'=9$), a polyethylene glycol #600 methacrylate ($m'=0$, $n'=14$) or the like, as represented by above general formula (9).

[0097]

The amount of the ethylenically unsaturated

addition-polymerizable monomer (c) (i.e., one or more types of compounds selected from the group consisting of an acrylate and a methacrylate) added is from 0.1 to 1,000 parts by mass, preferably from 1 to 500 parts by mass, more preferably from 2 to 200 parts by mass, and in view of heat resistance, most preferably from 5 to 100 parts by mass, per 100 parts by mass of the polyorganosiloxane (a).

[0098]

10 <Other Additives>

In order to provide a photosensitive resin composition having excellent characteristics in terms of light resistance of a molded article after curing, at least one compound selected from the group consisting of an ultraviolet absorber and a hindered amine-containing light stabilizer may be further added to the photosensitive resin composition of the present invention. In the case of adding such an additive, the amount thereof is, as the total amount of additives, preferably from 0.001 to 100 parts by mass, and in view of transparency and thermogravimetric loss, more preferably from 0.01 to 20 parts by mass, per 100 parts by mass of the polyorganosiloxane (a).

[0099]

25 In the case where the photosensitive resin composition contains an ultraviolet absorber or a hindered amine-containing light stabilizer, the amount added of the ultraviolet absorber or light stabilizer is preferably from 0.2 to 50 parts by mass, more preferably from 1 to 10 parts by mass, per 100 parts by mass of the polyorganosiloxane (a). When the amount added is 0.2 parts by mass or more, the ultraviolet absorber or light stabilizer is effective in enhancing the weather resistance and light resistance of the cured molded article, whereas when the amount added is 50 parts by mass or less, the light resistance and weather resistance can be enhanced while maintaining high transparency of

the photosensitive resin composition to which the ultraviolet absorber or light stabilizer is added and the cured molded article thereof.

[0100]

5 An adhesion aid, such as silane coupling agent may be further added to the photosensitive resin composition of the present invention, in order to provide a photosensitive resin composition holding high adherence to an inorganic material substrate, such as glass and
10 metal.

[0101]

 In particular, in view of cost and harmful effect, 3-glycidoxypyrpyltrimethoxysilane (KBM-403, available from Shin-Etsu Chemical Co., Ltd.), 3-
15 methacryloxypropyltrimethoxysilane (KBM-503, available from Shin-Etsu Chemical Co., Ltd.), and 3-aminopropyltriethoxysilane (KBE-903, available from Shin-Etsu Chemical Co., Ltd.) are preferred as the adhesion aid.

20 **[0102]**

 In the case of incorporating a silane coupling agent into the photosensitive resin composition, the amount added of the silane coupling agent is preferably from 1 to 100 parts by mass, more preferably from 10 to 50 parts
25 by mass, per 100 parts by mass of the polyorganosiloxane (a). When the amount added is 1 part by mass or more, a cured molded article having excellent adherence to an inorganic material substrate, such as glass and metal can be obtained.

30 **[0103]**

 If desired, a sensitizer for enhancing photosensitivity may be added to the photosensitive resin composition of the present invention.

 The sensitizer includes, for example, Michler's
35 ketone, 4,4'-bis(diethylamino)benzophenone, 2,5-bis(4'-diethylaminobenzylidene)cyclopentanone, 2,6-bis(4'-diethylaminobenzylidene)cyclohexanone, 2,6-bis(4'-

dimethylaminobenzylidene)-4-methylcyclohexanone, 2,6-bis(4'-diethylaminobenzylidene)-4-methylcyclohexanone, 4,4'-bis(dimethylamino)chalcone, 4,4'-bis(diethylamino)chalcone, 2-(4'-
5 dimethylaminocinnamylidene)indanone, 2-(4'-dimethylaminobenzylidene)indanone, 2-(p-4'-dimethylaminobiphenyl)benzothiazole, 1,3-bis(4-dimethylaminobenzylidene)acetone, 1,3-bis(4-diethylaminobenzylidene)acetone, 3,3'-carbonyl-bis(7-
10 diethylaminocoumarin), 3-acetyl-7-dimethylaminocoumarin, 3-ethoxycarbonyl-7-dimethylaminocoumarin, 3-benzyloxycarbonyl-7-dimethylaminocoumarin, 3-methoxycarbonyl-7-dimethylaminocoumarin, 3-ethoxycarbonyl-7-dimethylaminocoumarin, N-phenyl-N-ethylethanolamine, N-
15 phenyldiethanolamine, N-p-tolyldiethanolamine, N-phenylethanolamine, N,N-bis(2-hydroxyethyl)aniline, 4-morpholinobenzophenone, isoamyl 4-dimethylaminobenzoate, isoamyl 4-diethylaminobenzoate, benzotriazole, 2-mercaptobenzimidazole, 1-phenyl-5-mercapto-1,2,3,4-
20 tetrazole, 1-cyclohexyl-5-mercapto-1,2,3,4-tetrazole, 1-(tert-butyl)-5-mercapto-1,2,3,4-tetrazole, 2-mercaptobenzothiazole, 2-(p-dimethylaminostyryl)benzoxazole, 2-(p-dimethylaminostyryl)benzothiazole, 2-(p-
25 dimethylaminostyryl)naphtho(1,2-p)thiazole, 2-(p-dimethylaminobenzoyl)styrene, etc.

One of these compounds may be used alone, or a mixture of two or more thereof may be used.

In the case of adding a sensitizer to the
30 photosensitive resin composition, the amount added of the sensitizer depends on the amount of the other additive components, but is preferably from 0.1 to 10 parts by mass, more preferably from 1 to 5 parts by mass, per 100 parts by mass of the polyorganosiloxane (a).

35 **[0104]**

If desired, in order to enhance the viscosity stability or photosensitivity stability during storage, a

polymerization inhibitor may be added to the photosensitive resin composition of the present invention.

5 The polymerization inhibitor which can be used includes, for example, hydroquinone, N-nitrosodiphenylamine, p-tert-butylcatechol, phenothiazine, N-phenylnaphthylamine, ethylenediaminetetraacetic acid, 1,2-cyclohexanediaminetetraacetic acid, glycol ether
10 diaminetetraacetic acid, 2,6-di-tert-butyl-p-methylphenol, 5-nitroso-8-hydroxyquinoline, 1-nitroso-2-naphthol, 2-nitroso-1-naphthol, 2-nitroso-5-(N-ethyl-N-sulfopropylamino)phenol, N-nitroso-N-phenylhydroxylamine ammonium salt, N-nitroso-N-phenylhydroxylamine ammonium
15 salt, N-nitroso-N-(1-naphthyl)hydroxylamine ammonium salt, bis(4-hydroxy-3,5-di-tert-butyl)phenylmethane, etc.

In the case of adding a polymerization inhibitor to the photosensitive resin composition, the amount added of the polymerization inhibitor is preferably from 0.001 to
20 5 parts by mass, more preferably from 0.01 to 1 part by mass, per 100 parts by mass of the polyorganosiloxane (a).

[0105]

If desired, in order to enhance the thermal
25 stability in the presence of oxygen, an antioxidant may be added to the photosensitive resin composition of the present invention.

The antioxidant includes, for example, hindered phenolic antioxidant, phosphorus-based antioxidant,
30 lactone antioxidant, vitamin E antioxidant, sulfur-based antioxidant, etc.

Specific examples of the antioxidant include, but are not limited to, triethylene glycol-bis[3-(3-tert-butyl-5-methyl-4-hydroxyphenyl)propionate]
35 (IRGANOX(registered trademark) 245, produced by BASF), 1,6-hexanediol-bis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (IRGANOX(registered trademark)

259, produced by BASF), 2,4-bis-(n-octylthio)-6-(4-hydroxy-3,5-di-tert-butylanilino)-1,3,5-triazine (IRGANOX(registered trademark) 565, produced by BASF), pentaerythrityl-tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) (IRGANOX(registered trademark) 1010, produced by BASF), 2,2-thio-diethylenebis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (IRGANOX(registered trademark) 1035, produced by BASF), octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (IRGANOX(registered trademark) 1076, produced by BASF), N,N'-hexamethylenebis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide) (IRGANOX(registered trademark) 1098, produced by BASF), 3,5-di-tert-butyl-4-hydroxybenzylphosphonate-diethyl ester (IRGAMOD(registered trademark) 295, produced by BASF), 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene (IRGANOX(registered trademark) 1330, produced by BASF), tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-isocyanurate (IRGANOX(registered trademark) 3114, produced by BASF), octylated diphenylamine (IRGANOX(registered trademark) 5057, produced by BASF), 2,4-bis[(octylthio)methyl]-o-cresol (IRGANOX(registered trademark) 1520L, produced by BASF), isooctyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (IRGANOX(registered trademark) 1135, produced by BASF), 2,4-bis(dodecylthiomethyl)-6-methylphenol (IRGANOX(registered trademark) 1726, produced by BASF), 2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-ol (IRGANOX(registered trademark) E201, produced by BASF), 5,7-di-tert-butyl-3-(3,4-dimethylphenyl)benzofuran-2(3H)-one (IRGANOX(registered trademark) HP-136, produced by BASF), tris(2,4-di-tert-butylphenyl)phosphite (IRGAFOS(registered trademark) 168, produced by BASF), tris[2-[[2,4,8,10-tetrakis(1,1-dimethylethyl)dibenzo[d,f][1,3,2]dioxaphosphin-6-yl]oxy]ethyl]amine (IRGAFOS(registered trademark) 12, produced by BASF), bis(2,4-di-tert-butyl-6-

5 methylphenyl)ethylphosphite (IRGAFOS(registered
trademark) 38, produced by BASF), didodecyl 3,3-
thiobispropionate (IRGANOX(registered trademark) PS800,
produced by BASF), dioctadecyl 3,3-thiobispropionate
10 (IRGANOX(registered trademark) PS802, produced by BASF),
3,9-bis[2-[3-(3-tert-butyl-4-hydroxy-5-
methylphenyl)propionyloxy]-1,1-dimethylethyl]-2,4,8,10-
tetraoxaspiro[5.5]undecane (SUMILIZER(registered
trademark) GA-80, produced by Sumitomo Chemical), 2,2'-
10 methylenebis(6-tert-butyl-4-methylphenol)
(SUMILIZER(registered trademark) MDP-S, produced by
Sumitomo Chemical), 4,4'-butylidenebis(6-tert-butyl-3-
methylphenol) (SUMILIZER(registered trademark) BBM-S,
produced by Sumitomo Chemical), 4,4'-thiobis(6-tert-
15 butyl-3-methylphenol) (SUMILIZER(registered trademark)
WX-R, produced by Sumitomo Chemical), pentaerythryl
tetrakis(3-laurylthiopropionate) (SUMILIZER(registered
trademark) TP-D, produced by Sumitomo Chemical), 2-
mercaptobenzimidazole (SUMILIZER(registered trademark)
20 MB, produced by Sumitomo Chemical), biphenyl-4,4'-diyl
bis[bis(2,4-di-tert-butyl-5-methylphenoxy)phosphine]
(GSY-P101, produced by Osaki Industry), etc.

One of these antioxidants may be used alone, or a
mixture of two or more thereof may be used.

25 In the case of adding an antioxidant to the
photosensitive resin composition, the amount added of the
antioxidant is preferably from 0.001 to 30 parts by mass,
more preferably from 0.01 to 10 parts by mass, per 100
parts by mass of the polyorganosiloxane (a).

30 **[0106]**

If necessary, the photosensitive resin composition
of the present invention can be appropriately blended
with various additives, such as coating film smoothness-
imparting agent and inorganic fine particle as long as
35 the various additives do not inhibit various
characteristics required of the photosensitive resin
composition of the present invention.

[0107]

<Solvent>

A solvent can be added to the photosensitive resin composition of the present invention, so as to adjust the viscosity thereof. Suitable solvents include, for example, N,N-dimethylformamide, N-methyl-2-pyrrolidone (hereafter, sometimes referred to as "NMP"), N-ethyl-2-pyrrolidone, tetrahydrofuran, N,N-dimethylacetamide (hereafter, sometimes referred to as "DMAc"), dimethyl sulfoxide, hexamethylphosphoramide, pyridine, cyclopentanone, γ -butyrolactone (hereinafter, sometimes referred to as "GBL"), α -acetyl- γ -butyrolactone, tetramethylurea, 1,3-dimethyl-2-imidazolinone, N-cyclohexyl-2-pyrrolidone, propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, methyl ethyl ketone, methyl isobutyl ketone, anisole, ethyl acetate, ethyl lactate, butyl lactate, etc. One of these solvents may be used alone, or two or more thereof may be used in combination. Among these, N-methyl-2-pyrrolidone, γ -butyrolactone and propylene glycol monomethyl ether acetate are preferred.

The solvent may be appropriately added to the photosensitive resin composition depending on the coated film thickness and viscosity, but is preferably used in an amount of 0 to 200 parts by mass, per 100 parts by mass of the polyorganosiloxane (a).

[0108]

<Cured Product>

In an embodiment of the present invention, a cured product is obtained by photocuring the photosensitive resin composition of the present invention, or a photosensitive resin composition comprising the polyorganosiloxane (a) obtained by the above-described production process of a polyorganosiloxane, and the photopolymerization initiator (b).

[0109]

<Production Method of Molded Article>

The method for producing a molded article by using the photosensitive resin composition of the present invention is described below.

5 The molded article includes, for example, a microplastic lens or an optical element for a liquid crystal polarizing plate.

10 In the description of the present invention, a microplastic lens indicates a plastic fine lens having a diameter of generally several mm or less. A microlens array in which a number of microlenses each having a diameter of about tens of μm are arranged is used for enhancing light utilization efficiency in a CCD imaging element or an LCD projector, and a microlens having a
15 diameter of about hundreds of μm is used in an optical communication connector, a cellular phone camera module or the like.

[0110]

20 The optical element for a liquid crystal polarizing plate is referred to as a structure on a polarized light filter (polarizing plate) that is one member of a liquid crystal projector or liquid crystal display. In a liquid crystal panel, generally, a pair of polarized light filters (polarizing plates) is provided on the front and
25 back of a transparent substrate for enclosing a liquid crystal, and allows polarized light only in a given oscillating direction to pass therethrough. The liquid crystal polarizing plate can be produced, for example, by stretching a film and thereby orientating the composition thereof. A material having characteristics as a polarized
30 light filter can be also produced by forming a specific structure with a pitch of 0.2 to 0.3 μm on a substrate.

[0111]

35 The microplastic lens and the optical element for a liquid crystal polarizing plate differ only in the size and type, and the production methods for these two

members are the same. Specifically, the production method of a molded article of the present invention comprises:

- 5 1) a step of filling a shape-forming mold with the photosensitive resin composition of the present invention, or a photosensitive resin composition comprising (a) a polyorganosiloxane obtained by the above-described production process and (b) a photopolymerization initiator;
- 10 2) a step of pressing the opening of the mold against a substrate or another mold;
- 3) a step of exposing the photosensitive resin composition to light from the mold and/or substrate side to obtain a photocured product;
- 15 4) a step of separating the mold from the substrate, or separating the molds from both surfaces of the photocured product; and
- 5) a step of heating only the photocured product or the photocured product with the substrate.

20 **[0112]**

1) Step of filling a shape-forming mold with the photosensitive resin composition

 A shape-forming mold is filled with the photosensitive resin composition through the opening of the shape-forming mold.

 Alternatively, a shape-forming mold is filled with the photosensitive resin composition by dropping the photosensitive resin composition on a substrate or mold; and pressing a substrate or mold to the photosensitive resin composition make a stack of

30 "substrate/photosensitive resin composition/mold" or "mold/photosensitive resin composition/mold".

[0113]

 In the case of applying the photosensitive resin composition to the opening of the shape-forming mold, the photosensitive resin composition may be dropped in the opening by using a syringe or a dispenser.

35

In the case of coating the photosensitive resin composition on the substrate side, the photosensitive resin composition is dropped by using a syringe or dispenser, and then coated by a spin coater, a bar coater, a blade coater, a curtain coater, a screen printer or the like, or spray-coated by a spray coater or the like, to coat the composition on a substrate that is subjected, if desired, to coat the composition on a pretreated substrate, whereby a film of the photosensitive resin composition is formed.

[0114]

The thickness of the photosensitive resin composition is preferably from 0.01 to 10 mm, more preferably from 0.05 to 1 mm, still more preferably from 100 to 500 μm . When coating the photosensitive resin composition, the composition may be diluted with a solvent, such as NMP, but in this case, a step of removing the used solvent by heating is required. Heating the photosensitive resin composition is carried out by arranging the photosensitive resin composition thin film-formed surface of the coated substrate to face upward. As for a heating apparatus, any known apparatus, such as oven, far-infrared ray furnace and hot plate may be used as long as heating can be carried out. The heating conditions are from 50 to 150°C, preferably from 100 to 140°C, and for 1 to 30 minutes, preferably from 5 to 10 minutes. Incidentally, even in the case where the photosensitive resin composition is not diluted with a solvent, from the standpoint of increasing the adherence of the photosensitive resin composition to the substrate, a step of heating substrate with the photosensitive resin composition may be optionally added, and the apparatus used here is preferably a hot plate.

[0115]

As a pretreatment of the substrate, a silane coupling agent may be also optionally coated on the

substrate, so as to impart adherence property to the substrate. In the case of coating a substrate with a silane coupling agent, the silane coupling agent is diluted with an organic solvent, such as NMP, and is coated by using a spin coater, a bar coater, a blade coater, a curtain coater, a screen printer or the like, and thereafter, the solvent used is removed by heating. The heating is carried out by using a known apparatus, such as an oven, far infrared furnace or hot plate. Preferred chemical species of the silane coupling agent include, for example, 3-glycidoxypropyltrimethoxysilane (KBM-403, produced by Shin-Etsu Chemical), 3-methacryloxypropyltrimethoxysilane (KBM-503, produced by Shin-Etsu Chemical), 3-acryloxypropyltrimethoxysilane (KBM-5103, produced by Shin-Etsu Chemical), 3-aminopropyltriethoxysilane (KBE-903, produced by Shin-Etsu Chemical), etc.

[0116]

The substrate which can be used includes, for example, a glass substrate, a quartz substrate, a silicon substrate, and a copper substrate, such as copper clad laminate. In the case where the shape-forming mold is made of a material impermeable to light, a glass substrate or a quartz substrate is preferred.

[0117]

2) Step of pressing the opening of the shape-forming mold against a substrate or another mold

The opening of the shape-forming mold, for example, a microplastic lens mold or a mold for an optical element for a liquid crystal polarizing plate, is pressed against the thin-film formed surface of the substrate or another mold. At this time, a pressure may be applied, if desired. The shape-forming mold material includes rubber, glass, a resin, such as polydimethylsiloxane, and a metal, such as Ni, and among others, a transparent resin is preferred.

[0118]

In the production method of a molded article of the present invention, in the case of pressing the opening of the mold against the substrate, a step of applying a silane coupling agent on the substrate is preferably added before a step of pressing the opening of the mold against the substrate, and the opening of the mold is preferably pressed against the silane coupling agent-applied surface of the substrate during the step of pressing the opening of the mold against the substrate.

10 **[0119]**

3) Step of exposing the photosensitive resin composition to light from the mold and/or substrate side to obtain a photocured product

15 In the state of sandwiching the photosensitive resin composition between a substrate and a shape-forming mold, the photosensitive resin composition is irradiated with an ultraviolet ray from the side of the shape-forming mold or substrate which is formed of a material permeable to the exposure light.

20 If desired, the photosensitive resin composition may be irradiated with an ultraviolet ray from both sides of a laminate which is in the state of sandwiching the photosensitive resin composition between a substrate and a shape-forming mold or between a mold and a mold. In view of pattern resolution and handleability as the photocuring resin, the wavelength of the exposure light source is preferably i-line.

25 **[0120]**

30 4) Step of separating the mold from the substrate or separating the molds from both surfaces of the photosensitive resin composition

35 After curing the photosensitive resin composition with ultraviolet light, the shape-forming mold is separated from the substrate, or the molds on both surfaces of the photosensitive resin composition are separated.

[0121]

5) Step of heating only the photocured product or the photocured product with the substrate (PEB treatment)

The remaining reactive groups are bonded by heating the photocured product at a temperature of 150 to 270°C for 5 seconds to 5 hours, whereby a molded article excellent in the heat resistance, for example, a microplastic lens or an optical element for a liquid crystal polarizing plate, can be obtained. The heating may be performed by using a hot plate, an oven, or a temperature-programmed oven capable of setting a temperature program. The atmosphere gas during heating may be air, but it is preferable to use an inert gas, such as nitrogen and argon. Incidentally, this heating step is a step that can be optionally added so as to increase the hardness of the molded article, for example, a microplastic lens or an optical element for a liquid crystal polarizing plate.

[0122]

By performing the steps described above, the molded article of the present invention is obtained.

[0123]

<Method for Forming Cured Relief Pattern and Polyorganosiloxane Film>

An example of the method for forming a cured relief pattern by using the photosensitive resin composition of the present invention is described below. The production method of a cured relief pattern comprises:

1) a step of coating the photosensitive resin composition of the present invention or a photosensitive resin composition containing (a) a polyorganosiloxane obtained by the production process of a polyorganosiloxane of the present invention and (b) a photopolymerization initiator to obtain a coated film,

2) a step of irradiating the coated film with an active ray to photocure the exposed area of the film,

3) a step of removing the uncured portion of the film by using a developer, and

4) a step of heating the cured portion with the substrate material.

[0124]

5 1) Step of coating the photosensitive resin composition of the present invention to obtain a coated film

First, the photosensitive resin composition of the present invention is coated on a silicon wafer, a ceramic substrate, an aluminum substrate or other various desired substrates. As for the coating apparatus or coating method, a spin coater, a die coater, a spray coater, 10 dipping, printing, a blade coater, roll coating and the like may be utilized. The substrate coated with the photosensitive resin composition is soft-baked at 80 to 200°C for a time of 10 seconds to 1 hour.

15 **[0125]**

2) Step of irradiating the coated film with an active ray to photocure the exposed area of the film

The coated film is irradiated with an actinic ray through a desired photomask by using an exposure 20 projection apparatus, such as contact aligner, mirror projection and stepper. As the active ray, an X-ray, an electron beam, an ultraviolet ray, a visible light ray and the like may be utilized, but in the present invention, an active ray having a wavelength of 200 to 25 500 nm is preferably used. In view of pattern resolution and handleability, the light source wavelength is preferably a UV-i line (365 nm), and a stepper is preferred as the exposure projection apparatus.

[0126]

30 After step 2), for the purpose of enhancing the photosensitivity or the like, a post-exposure baking (PEB) or a pre-development baking may be performed, if desired, by optionally combining the temperature and the time (preferably a temperature of 40 to 200°C and a time 35 of 10 seconds to 30 minutes).

[0127]

3) Step of removing the uncured portion of the film by

using a developer

This step can be carried out by a method, such as dipping method, puddling method and rotating spray method. As the developer, a good solvent for the photosensitive resin composition of the present invention may be used alone, or a good solvent and a poor solvent may be appropriately mixed and used. The good solvent includes, for example, N-methyl-2-pyrrolidone, N-acetyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide, dimethyl sulfoxide, gamma-butyrolactone, α -acetyl-gamma-butyrolactone, cyclopentanone, cyclohexanone, propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, methyl ethyl ketone, and methyl isobutyl ketone. The poor solvent includes, for example, methanol, ethanol, isopropanol, and water.

[0128]

After the completion of development, washing is performed with a rinsing solution to remove the developer, whereby a coating film with a relief pattern is obtained. As the rinsing solution, distilled water, methanol, ethanol, isopropanol, propylene glycol monomethyl ether and the like may be used alone or as an appropriate mixture or may be used by stepwise combining these.

[0129]

4) Step of heating the cured portion with the substrate material ((final) heating step, PEB treatment)

The relief pattern obtained as above is converted to a cured relief pattern at 150 to 260°C. The heat curing may be performed by using a hot plate, an inert oven, a temperature-programmed oven capable of setting a temperature program, or the like. The atmosphere gas during heat curing may be air, or an inert gas, such as nitrogen and argon may be used, if desired.

[0130]

The cured relief pattern obtained by the production

method above is used as any one member selected from the group consisting of a surface protective film, an interlayer insulating film and an α -ray shielding film of a semiconductor device formed on a substrate, such as silicon wafer, and a support (partition wall) between a microstructure, such as microlens array and a package material thereof, and further subjected to other steps in the known manufacturing method of a semiconductor device, whereby a variety of semiconductor devices including an optical element, such as CMOS image sensor can be manufactured. An electronic component or semiconductor device having a coating film composed of a resin obtained by curing the photosensitive resin composition can also be produced.

EXAMPLES

[0131]

The present invention is explained in greater detail below by referring to Examples, but the scope of the present invention is not limited thereto.

[Example 1]

Photosensitive Resin Composition:

A 2-L separable flask was charged with 1.37 mol (275 g) of dicyclopentylsilanediol as the silanol compound, 1.37 mol (341 g) of $(\text{CH}_3\text{O})_3\text{-Si-}(\text{CH}_2)_3\text{-O-C(=O)-C(CH}_3\text{)=CH}_2$ as the alkoxysilane compound and 0.00858 mol (1.63 g) of $\text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$ as the catalyst, and equipped with a Liebig condenser for removing the alcohol produced, and in this state, the mixture was gradually heated from room temperature to 50°C in an oil bath under reduced pressure of 500 hPa. Since the initiation of reaction, when the reaction solution became transparent (that is, the dicyclopentylsilanediol was dissolved), the pressure was reduced to 250 hPa. Methanol generated by keeping the stirring was cooled by the Liebig condenser and liquefied, and after confirming that the liquefied methanol began discharging to the outside of the system,

the reaction was further continued for 2 hours. The degree of vacuum was gradually raised to avoid occurrence of bumping at the same temperature as that in the pressure reduction, and while further removing the methanol at 8 to 15 hPa, the reaction was continued for 2 hours. Finally, the system was returned to the atmospheric pressure to terminate the removal of methanol. The obtained white cloudy viscous liquid was dissolved in cyclohexane and then filtered, and the solvent was removed by an evaporator. Subsequently, vacuum suction was performed at 80°C for 30 minutes. After standing to cool, when the system was returned to room temperature, an operation of adding methanol to the system, stirring the mixture and removing the supernatant was repeated three times. Remains methanol from the obtained methanol-insoluble part was removed by using an evaporator at 60°C, and the residue was dried at 80°C for 1 hour and 30 minutes. The weight average molecular weight of the obtained polyorganosiloxane was 5,329. In the obtained polyorganosiloxane, 30% by number of Si atoms were contained in the structure represented by above general formula (2) (in the formula, X was $-(CH_2)_3-$ (based on ^{13}C -NMR spectrum). In the 1H -NMR spectrum, the peak derived from a carboxylic acid of the ester moiety was decreased by 31%, and in the GPC chart, the area having a weight average molecular weight of 1,050 or more was 83% of the whole GPC peak area (Figs. 1, 2 and 3).

[0132]

2 Parts by mass of radical photopolymerization initiator DAROCURE(registered trademark) 1173 (produced by BASF) was added per 100 parts by mass of the polyorganosiloxane to obtain a photosensitive resin composition.

[0133]

The decrease ratio of the peak derived from a carboxylic acid of the ester moiety was calculated by comparison between $-C=CH_2$ and $Si-CH_2-$ of $(CH_3O)_3Si-(CH_2)_3-$

$\text{O}-(\text{C}=\text{O})-\text{C}(\text{CH}_3)=\text{CH}_2$ in the ^1H -NMR spectrum.

[0134]

[Example 2]

Photosensitive Resin Composition:

5 Synthesis of a polyorganosiloxane was carried out in
the same manner as in Example 1, except that $(\text{CH}_3\text{O})_3\text{-Si-}$
 $(\text{CH}_2)_3\text{-O}-(\text{C}=\text{O})-\text{CH}=\text{CH}_2$ was used in place of $(\text{CH}_3\text{O})_3\text{-Si-}$
 $(\text{CH}_2)_3\text{-O}-(\text{C}=\text{O})-\text{C}(\text{CH}_3)=\text{CH}(\text{CH}_3)$ used in Example 1 and reacted
for 75 minutes, and as the solvent for washing the
10 obtained polyorganosiloxane, acetonitrile was used in
place of methanol. The weight average molecular weight
of the obtained polyorganosiloxane was 1,582. In the
obtained polyorganosiloxane, 27% by number of Si atoms
were contained in the structure represented by above
15 general formula (2), and X was $-(\text{CH}_2)_3-$ (based on ^{13}C -NMR
spectrum). In the ^1H -NMR spectrum, the peak derived from
a carboxylic acid of the ester moiety was decreased by
29% (Fig. 4). 2 Parts by mass of radical
photopolymerization initiator Lucirin (registered
20 trademark) TPO (produced by BASF) was added per 100 parts
by mass of the obtained polyorganosiloxane to obtain a
photosensitive resin composition.

[0135]

25 The decrease ratio of the peak derived from a
carboxylic acid of the ester moiety was calculated by
comparison between $-\text{CH}=\text{CH}_2$ (the peaks near 5.80 ppm, 6.10
ppm and 6.37 ppm) and $\text{Si}-\text{CH}_2-$ (the peak near 0.65 ppm) of
 $(\text{CH}_3\text{O})_3\text{-Si-}(\text{CH}_2)_3\text{-O}-(\text{C}=\text{O})-\text{CH}=\text{CH}_2$ in the ^1H -NMR spectrum.

[0136]

30 [Example 3]

Photosensitive Resin Composition:

35 Synthesis was carried out in the same manner as in
Example 2, except for changing the reaction time of
Example 2 to 60 minutes. The weight average molecular
weight of the obtained polyorganosiloxane was 1,495. In
the obtained polyorganosiloxane, 21% by number of Si
atoms were contained in the structure represented by

above general formula (2), and X was $-(CH_2)_3-$ (based on ^{13}C -NMR spectrum). In the 1H -NMR spectrum, the peak derived from a carboxylic acid of the ester moiety was decreased by 22%.

5 **[0137]**

[Example 4]

Photosensitive Resin Composition:

Synthesis was carried out in the same manner as in Example 2, except for changing the reaction time of
10 Example 2 to 45 minutes. The weight average molecular weight of the obtained polyorganosiloxane was 1,380. In the obtained polyorganosiloxane, 12% by number of Si atoms were contained in the structure represented by above general formula (2), and X was $-(CH_2)_3-$. In the 1H -
15 NMR spectrum, the peak derived from a carboxylic acid of the ester moiety was decreased by 13%.

[0138]

[Example 5]

Photosensitive Resin Composition:

20 Synthesis was carried out in the same manner as in Example 2, except for changing the reaction time of Example 2 to 30 minutes. The weight average molecular weight of the obtained polyorganosiloxane was 1,260. In the obtained polyorganosiloxane, 9% by number of Si atoms
25 were contained in the structure represented by above general formula (2), and X was $-(CH_2)_3-$ (based on ^{13}C -NMR spectrum). In the 1H -NMR spectrum, the peak derived from a carboxylic acid of the ester moiety was decreased by 9%.

30 **[0139]**

[Example 6]

Photosensitive Resin Composition:

A photosensitive resin composition was obtained by carrying out the same processing as in Example 1, except
35 that after cooling the photosensitive resin of Example 1 to room temperature, 5 mass% of A-600 (produced by Shin-Nakamura Chemical) and 45 mass% of A-DCP (produced by

Shin-Nakamura Chemical) were added together with the radical photopolymerization initiator.

[0140]

[Example 7]

5 Photosensitive Resin Composition:

 A photosensitive resin composition was obtained by carrying out the same processing as in Example 2, except that after cooling the photosensitive resin of Example 2 to room temperature, 10 mass% of A-600 (produced by Shin-Nakamura Chemical) and 5 mass% of A-DCP (produced by Shin-Nakamura Chemical) were added together with the radical photopolymerization initiator.

[0141]

[Example 8]

15 Photosensitive Resin Composition:

 A 2-L separable flask was charged with 0.2 mol (49.8 g) of $(\text{CH}_3\text{O})_3\text{-Si-(CH}_2)_3\text{-O-(C=O)-CH=CH}_2$ as the alkoxysilane compound, 0.001 mol (0.19 g) of $\text{Ba(OH)}_2 \cdot \text{H}_2\text{O}$ as the catalyst and 0.18 mol (3.24 g) of water, and equipped with a Liebig condenser for removing the alcohol produced, and in this state, the mixture was gradually heated from room temperature to 50°C in an oil bath under reduced pressure of 250 hPa. Methanol generated by keeping the stirring was cooled by the Liebig condenser and liquefied, and after confirming that the liquefied methanol began discharging to the outside of the system, the reaction was further continued for 2 hours. Thereafter, the reaction temperature was gradually raised to 80°C and the reaction was further allowed to proceed for 2 hours. Subsequently, the degree of vacuum was gradually raised to avoid occurrence of bumping, and while further removing the methanol at 8 to 15 hPa, the reaction was continued for 2 hours. Finally, the system was returned to the atmospheric pressure to terminate the removal of methanol. The obtained white cloudy viscous liquid was dissolved in cyclohexane and then filtered, and the solvent was removed by an evaporator.

Furthermore, vacuum suction was performed at 80°C for 30 minutes. After standing to cool, when the system was returned to room temperature, an operation of adding methanol, stirring the mixture and removing the supernatant was repeated three times. Remains methanol from the obtained methanol-insoluble part was removed by using an evaporator at 60°C, and the residue was dried at 80°C for 1 hour and 30 minutes. The weight average molecular weight of the obtained polyorganosiloxane was 5,256. In the obtained polyorganosiloxane, 14% by number of Si atoms were contained in the structure represented by above general formula (2), and X was $-(CH_2)_3-$ (based on ^{13}C -NMR spectrum). In the 1H -NMR spectrum, the peak derived from a carboxylic acid of the ester moiety was decreased by 16%.

[0142]

[Comparative Example 1]

Photosensitive Resin Composition:

A 300-mL separable flask was charged with 0.150 mol (30.0 g) of dicyclopentylsilanediol as the silanol compound, 0.15 mol (37.2 g) of $(CH_3O)_3Si-(CH_2)_3O-(C=O)-C(CH_3)=CH_2$ as the alkoxysilane compound and 0.0003 mol (0.0945 g) of $Ba(OH)_2 \cdot H_2O$ as the catalyst, and equipped with a Liebig condenser for removing the alcohol produced, and in this state, the mixture was gradually heated from room temperature to 50°C in an oil bath under reduced pressure of 500 hPa. Since the initiation of reaction, when the reaction solution became transparent (that is, the dicyclopentylsilanediol was dissolved), the pressure was reduced to 250 hPa. Methanol generated by keeping the stirring was cooled by the Liebig condenser and liquefied, and after confirming that the liquefied methanol began discharging to the outside of the system, the reaction was further continued for 2 hours. The degree of vacuum was gradually raised to avoid occurrence of bumping at the same temperature as that in the

pressure reduction, and while further removing the methanol at 8 to 15 hPa, the reaction was continued for 2 hours. Finally, the system was returned to the atmospheric pressure to terminate the removal of methanol. The obtained white cloudy viscous liquid was dissolved in cyclohexane and then filtered, and the solvent was removed by an evaporator. Subsequently, vacuum suction was carried out at 80°C for 30 minutes. The weight average molecular weight of the obtained polyorganosiloxane was 1,002. In the obtained polyorganosiloxane, 1% or less by number of Si atoms were contained in the structure represented by above general formula (2), and X was $-(CH_2)_3-$ (based on ^{13}C -NMR spectrum). In the 1H -NMR spectrum, the decrease ratio of the peak derived from a carboxylic acid of the ester moiety was 1% or less. 2 Parts by mass of radical photopolymerization initiator Lucirin (registered trademark) TPO (produced by BASF) was added per 100 parts by mass of the obtained polyorganosiloxane to obtain a photosensitive resin composition.

[0143]

[Performance Comparison Result 1]

The performance of a cured film obtained by sandwiching each of the resin compositions obtained in Examples 1 to 8 and Comparative Example 1 between glass substrates, and under the condition of a diameter of 10 mm and a thickness of 500 μm , performing exposure of 3,000 mJ/cm^2 is shown in Table 1 below. In the evaluation of thermal shock(crack, peeling) resistance, a cold-heat cycle test (a test of alternately repeating standing for 15 minutes in an atmosphere of +125°C and standing for 15 minutes in an atmosphere of -40°C) was carried out by using TSE-11 manufactured by ESPEC Corp., and the presence or absence of cracks generated in the resin deposited as a film on the glass substrate and the presence or absence of film peeling were inspected by

eye. Ratings are:

A: no crack in the resin and no film peeling even after 100 cold-heat cycles,

5 B: no crack in the resin and no film peeling after 10 cold-heat cycles, but cracks and film peeling were observed after 100 cycles, and

C: cracks and film peeling were observed after 10 cold-heat cycles.

[0144]

10 [Table 1]

	Example 1	Example 2	Example 3	Example 4
Percentage of Si bonds forming $\equiv\text{Si-O-X-Si}\equiv$ bond (%)	30	27	21	12
Decrease ratio of peak area derived from carboxylic acid in $^1\text{H-NMR}$ spectrum (%)	31	29	22	13
Thermal shock resistance*	A	A	A	B

	Example 5	Example 6	Example 7	Example 8	Comparative Example 1
Percentage of Si bonds forming $\equiv\text{Si-O-X-Si}\equiv$ bond (%)	9	30	27	14	<1
Decrease ratio of peak area derived from carboxylic acid in $^1\text{H-NMR}$ spectrum (%)	9	31	29	16	<1
Thermal shock resistance*	B	A	A	B	C

*Cold-heat cycle test: A indicates >100 cycles, B indicates from 10 to 100 cycles, and C indicates <10 cycles.

15

[0145]

[Example 9]

Photosensitive Resin Composition:

20 Synthesis was carried out in the same manner as in Example 1, except for changing the reaction temperature to 95°C, the reaction pressure to atmospheric pressure, the reaction time to 30 minutes, the drying temperature

to 130°C, and the drying time to 30 minutes, respectively in Example 1. The weight average molecular weight of the obtained polyorganosiloxane was 7,830. In the obtained polyorganosiloxane, 48% by number of Si atoms were
5 contained in the structure represented by above general formula (2), and X was $-(CH_2)_3-$. In the 1H -NMR spectrum, the peak derived from a carboxylic acid of the ester moiety was decreased by 54%, and in the GPC chart, the area having a weight average molecular weight of 1,050 or
10 more was 89% (Figs. 5 and 6).

[0146]

[Example 10]

Photosensitive Resin Composition:

A photosensitive resin composition was obtained by
15 carrying out the same processing as in Example 1, except that after cooling the photosensitive resin of Example 1 to room temperature, 50 mass% of dicyclopentanyloxy acrylate (FA-513AS, produced by Hitachi Chemical) was added together with the radical photopolymerization
20 initiator.

[0147]

[Comparative Example 2]

Photosensitive Resin Composition:

A photosensitive resin composition was obtained by
25 using a polyorganosiloxane synthesized according to the method described in Synthesis Example 1 of Patent Document 3, by means of the same method as in Example 1.

[0148]

[Performance Comparison Result 2]

30 The performance of a cured film obtained by sandwiching each of the resin compositions obtained in Examples 1, 6, 9 and 10 and Comparative Example 2 between glass substrates, and under the condition of a diameter of 10 mm and a thickness of 500 μm , performing exposure
35 of 3,000 mJ/cm^2 is shown in Table 2 below. In the evaluation of thermal shock(crack, peeling) resistance, a cold-heat cycle test (a test of alternately repeating

standing for 15 minutes in an atmosphere of +125°C and standing for 15 minutes in an atmosphere of -40°C) was carried out, and the presence or absence of cracks generated in the resin deposited as a film on the glass substrate and the presence or absence of film peeling were inspected by eye. Ratings are:

A: no crack in the resin and no film peeling even after 100 cold-heat cycles, and

B: cracks in the resin and film peeling were observed after 100 cycles.

[0149]

[Table 2]

Table 2

	Example 1	Example 6	Example 9	Example 10	Comparative Example 2
Molecular weight	5329	5329	7830	5329	6629
Content percentage of high molecular weight ¹⁾	83%	83%	89%	83%	67%
Thermal shock resistance*	A	A	A	A	B

*Cold-heat cycle test: A indicates >100, and B indicates <100.

¹⁾: The content percentage of high molecular weight indicates the area of portions having a weight average molecular weight of 1,050 or more in the chart by RI detector of GPC.

[0150]

[Example 11]

Photosensitive Resin Composition:

A photosensitive resin composition was obtained by performing the same processing as in Example 7, except that 0.28 parts by mass of antioxidant IRGANOX(registered trademark) 245 (produced by BASF) and 0.11 parts by mass of antioxidant GSY-P101 (produced by Osaki Industry) were further added to the photosensitive resin composition of Example 7.

A sample was produced by stripping off one glass

substrate from a cured film which was obtained by sandwiching each of the resin compositions obtained in Examples 7 and 11 between glass substrates, and under the condition of a thickness of 500 μm , performing exposure of 3,000 mJ/cm^2 . The transmittance for light at a wavelength of 400 nm when the obtained sample was subjected to a heat treatment at 150°C for 13 hours in nitrogen or in a nitrogen atmosphere having an oxygen concentration of 7% (treatment in nitrogen is designated as A1 and that in an atmosphere with 7% of oxygen is designated as A2), and the transmittance for light at 400 nm when the heat-treated sample above was further subjected to a heat treatment (B) in nitrogen at 260°C for 10 seconds three times, are shown in Table 3 below. The transmittance of the cured film was measured by using an ultraviolet-visible spectrophotometer V-550 manufactured by JASCO with reference to an untreated glass substrate. It is seen that the photosensitive resin composition of Example 10 where an antioxidant was added, is improved in the thermal stability in the presence of oxygen.

[0151]

[Table 3]

Table 3

	Example 7, Transmittance (%)	Example 11, Transmittance (%)
Heat treatment (A1)	96	97
Heat treatments (A1)+(B)	96	96
Heat treatment (A2)	83	94
Heat treatments (A2)+(B)	78	93

INDUSTRIAL APPLICABILITY

[0152]

According to the present invention, a photosensitive transparent resin composition having excellent thermal shock resistance in the production of products with integrated electronic parts or solid-state imaging elements that requires a reflow soldering process at 260°C, can be obtained, and in turn, a plastic lens or an

optical element for a liquid crystal polarizing plate for a projector, each requiring heat resistance, can be obtained.

CLAIMS

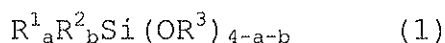
[Claim 1]

A photosensitive resin composition comprising:

5 (a) 100 parts by mass of a polyorganosiloxane having a polymerizable functional group; and

(b) from 0.01 to 30 parts by mass of a photopolymerization initiator;

wherein the polyorganosiloxane is obtained by means of a method of mixing at least one alkoxysilane compound represented by following general formula (1):



{wherein R^1 is an ester bond-containing organic group having a carbon number of 2 to 17, and at least one R^1 has an acryloyl group or a methacryloyl group; R^2 is, when a plurality of R^2 s are present, each is independently, an aliphatic group having a carbon number of 1 to 10, which may have a substituent; R^3 is, when a plurality of R^3 s are present, each is independently, a methyl group or an ethyl group; a is an integer of 1 or 2; b is an integer of 0, 1 or 2; and a+b is 3 or less}

15 and a catalyst to obtain a mixture, and polymerizing the mixture,

wherein the polyorganosiloxane contains a structure represented by following general formula (2):



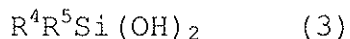
{wherein X is an organic group having a carbon number of 1 to 15}, and

wherein from 5 to 60% by number of Si atoms in the polyorganosiloxane are contained in the structure represented by general formula (2).

[Claim 2]

The photosensitive resin composition according to claim 1, wherein the polyorganosiloxane is obtained by means of a method of mixing the at least one alkoxysilane compound represented by general formula (1), at least one silanol compound represented by following general formula (3):

35



{wherein each of R^4 and R^5 is an aliphatic, alicyclic or aromatic group having a carbon number of 3 to 10, which may have a substituent} and a catalyst to obtain a mixture, and polymerizing the mixture.

[Claim 3]

The photosensitive resin composition according to claim 1 or 2, wherein from 10 to 40% by number of Si atoms in the polyorganosiloxane are contained in the structure represented by general formula (2).

[Claim 4]

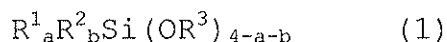
A photosensitive resin composition comprising:

(a) 100 parts by mass of a polyorganosiloxane; and

(b) from 0.01 to 30 parts by mass of a

photopolymerization initiator;

wherein the polyorganosiloxane is obtained by means of a method of mixing at least one alkoxysilane compound represented by following general formula (1):

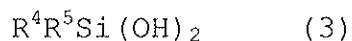


{wherein R^1 is an ester bond-containing organic group having a carbon number of 2 to 17, and at least one R^1 has an acryloyl group or a methacryloyl group; R^2 is, when a plurality of R^2 s are present, each is independently, an aliphatic group having a carbon number of 1 to 10, which may have a substituent; R^3 is, when a plurality of R^3 s are present, each is independently, hydrogen, a methyl group or an ethyl group; a is an integer of 1 or 2; b is an integer of 0, 1 or 2; and $a+b$ is 3 or less} and a catalyst to obtain a mixture, and polymerizing the mixture, and

wherein the ratio of the peak area derived from a carboxylic acid of the ester bond and the peak area derived from an alcohol of the ester bond in the polyorganosiloxane by 1H -NMR spectrum is decreased by 5 to 60% compared to the mixture of the alkoxysilane compound before polymerization.

[Claim 5]

The photosensitive resin composition according to claim 4, wherein the polyorganosiloxane is obtained by means of a method of mixing the at least one alkoxysilane compound represented by general formula (1), at least one silanol compound represented by following general formula (3):



{wherein each of R^4 and R^5 is an aliphatic, alicyclic or aromatic group having a carbon number of 3 to 10, which may have a substituent} and a catalyst to obtain a mixture, and polymerizing the mixture.

[Claim 6]

The photosensitive resin composition according to claim 4 or 5, wherein the ratio of the peak area derived from a carboxylic acid of the ester bond and the peak area derived from an alcohol of the ester bond in the 1H -NMR spectrum of the polyorganosiloxane is decreased by 10 to 40% compared to the mixture of the alkoxysilane compound and the silanol compound before polymerization.

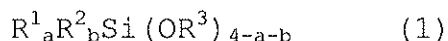
[Claim 7]

A photosensitive resin composition comprising:

(a) 100 parts by mass of a polyorganosiloxane; and

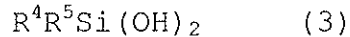
(b) from 0.01 to 30 parts by mass of a photopolymerization initiator;

wherein the polyorganosiloxane is obtained by means of a method of mixing at least one alkoxysilane compound represented by following general formula (1):



{wherein R^1 is an ester bond-containing organic group having a carbon number of 2 to 17, and at least one R^1 has an acryloyl group or a methacryloyl group; R^2 is, when a plurality of R^2 s are present, each is independently, an aliphatic group having a carbon number of 1 to 10, which may have a substituent; R^3 is, when a plurality of R^3 s are present, each is independently, a methyl group or an ethyl group; a is an integer of 1 or 2; b is an integer of 0, 1 or 2; and $a+b$ is 3 or less},

at least one silanol compound represented by following general formula (3):

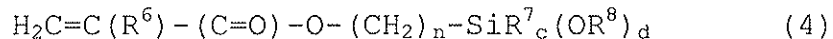


5 {wherein each of R^4 and R^5 is an aliphatic, alicyclic or aromatic group having a carbon number of 3 to 10, which may have a substituent} and a catalyst to obtain a mixture, and polymerizing the mixture, and

wherein an area having a weight average molecular weight of 1,050 or more in terms of standard polystyrene as measured by gel permeation chromatography (GPC) is 70% or more of the whole GPC peak area.

[Claim 8]

The photosensitive resin composition according to any one of claims 1 to 7, wherein the alkoxyasilane
15 compound represented by general formula (1) is at least one alkoxyasilane compound represented by following general formula (4):



20 {wherein R^6 is hydrogen or a methyl group; R^7 is, when a plurality of R^7 s are present, each is independently, an aliphatic group having a carbon number of 1 to 10, which may have a substituent; R^8 is, when a plurality of R^8 s are present, each is independently, a methyl group or an ethyl group; c is an integer of 0, 1 or 2; d is an integer of 1, 2 or 3; $c+d$ is 3 or less; and n is from 1 to 14}.

[Claim 9]

The photosensitive resin composition according to any one of claims 2, 3 and 5 to 8, wherein at least one
30 of R^4 and R^5 in general formula (3) is an alicyclic group having a carbon number of 3 to 10, which may have a substituent.

[Claim 10]

The photosensitive resin composition according to
35 any one of claims 1 to 9, further comprising (c) from 0.1 to 1,000 parts by mass of an ethylenically unsaturated addition-polymerizable monomer per 100 parts by mass of

the polyorganosiloxane.

[Claim 11]

5 The photosensitive resin composition according to claim 10, wherein the ethylenically unsaturated addition-polymerizable monomer is a compound containing an alicyclic group.

[Claim 12]

10 The photosensitive resin composition according to any one of claims 1 to 11, further comprising at least one additive selected from the group consisting of an ultraviolet absorber, a light stabilizer, an adhesion aid, a polymerization inhibitor, a sensitizer, an antioxidant and a smoothness-imparting agent.

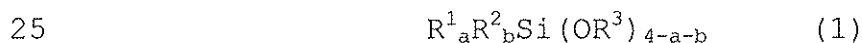
[Claim 13]

15 The photosensitive resin composition according to any one of claims 1 to 12, wherein the concentration of the alkali metal or alkaline earth metal in the photosensitive resin composition is from 0.1 to 500 ppm.

[Claim 14]

20 A production process of a polyorganosiloxane, comprising the following steps of:

i) producing (a) a polyorganosiloxane by mixing at least one alkoxysilane compound represented by following general formula (1):



30 {wherein R^1 is an ester bond-containing organic group having a carbon number of 2 to 17, and at least one R^1 has an acryloyl group or a methacryloyl group; R^2 is, when a plurality of R^2 s are present, each is independently, an aliphatic group having a carbon number of 1 to 10, which may have a substituent; R^3 is, when a plurality of R^3 s are present, each is independently, a methyl group or an ethyl group; a is an integer of 1 or 2; b is an integer of 0, 1 or 2; and a+b is 3 or less},
35 from 0.01 to 0.5 equivalents of water per one equivalent of OR^3 contained in the alkoxysilane compound present in the reaction system, and a catalyst to obtain a mixture,

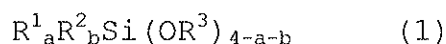
and reacting the mixture at 20 to 130°C for 0.1 to 20 hours while removing an alcohol produced by the reaction from the reaction system; and

5 ii) washing the polyorganosiloxane with a solvent incapable of dissolving the polyorganosiloxane.

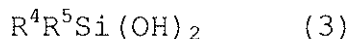
[Claim 15]

A production process of a polyorganosiloxane, comprising the following steps of:

10 i) producing (a) a polyorganosiloxane by mixing at least one alkoxysilane compound represented by following general formula (1):



15 {wherein R^1 is an ester bond-containing organic group having a carbon number of 2 to 17, and at least one R^1 has an acryloyl group or a methacryloyl group; R^2 is, when a plurality of R^2 s are present, each is independently, an aliphatic group having a carbon number of 1 to 10, which may have a substituent; R^3 is, when a plurality of R^3 s are present, each is independently, a
20 methyl group or an ethyl group; a is an integer of 1 or 2; b is an integer of 0, 1 or 2; and a+b is 3 or less}, at least one silanol compound represented by following general formula (3):



25 {wherein each of R^4 and R^5 is an aliphatic, alicyclic or aromatic group having a carbon number of 3 to 10, which may have a substituent} and a catalyst to obtain a mixture, and reacting the mixture at 20 to 130°C for 0.1 to 20 hours while removing an alcohol produced by
30 the reaction from the reaction system; and

ii) washing the polyorganosiloxane with a solvent incapable of dissolving the polyorganosiloxane.

[Claim 16]

35 The production process according to claim 14 or 15, wherein the catalyst is at least one compound selected from the group consisting of an alkali metal hydroxide and an alkaline earth metal hydroxide.

[Claim 17]

The production process according to any one of claims 14 to 16, wherein the catalyst is $\text{Ba}(\text{OH})_2$ and/or a hydrate thereof.

5 [Claim 18]

The production process according to any one of claims 14 to 17, wherein the amount of the catalyst is from 0.05 to 30 mol% based on a total number of moles of silicon (Si).

10 [Claim 19]

The production process according to any one of claims 14 to 18, wherein the amount of the catalyst is from 0.1 to 10 mol% based on a total number of moles of silicon (Si).

15 [Claim 20]

The production process according to any one of claims 14 to 19, wherein the solvent is an alcohol or an acetonitrile.

[Claim 21]

20 A cured product obtained by photocuring the photosensitive resin composition according to any one of claims 1 to 13, or a photosensitive resin composition comprising (a) a polyorganosiloxane obtained by the production process according to any one of claims 14 to
25 20 and (b) a photopolymerization initiator.

[Claim 22]

A method for producing a molded article, comprising the following steps of:

30 filling a shape-forming mold with the photosensitive resin composition according to any one of claims 1 to 13, or a photosensitive resin composition comprising (a) a polyorganosiloxane obtained by the production process according to any one of claims 14 to 20 and (b) a photopolymerization initiator,

35 pressing the opening of the mold against a substrate or another mold,

exposing the photosensitive resin composition to

light from the mold and/or substrate side to obtain a photocured product,

separating the mold from the substrate, or
separating the molds from both surfaces of the photocured
product, and

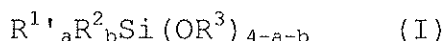
heating only the photocured product, or the
photocured product with the substrate.

[Claim 23]

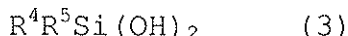
A molded article obtained by the method according to
claim 22.

[Claim 24]

A polyorganosiloxane obtained by means of a method
of mixing at least one alkoxyasilane compound represented
by following general formula (I):

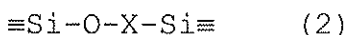


{wherein $R^{1'}$ is an ester bond-containing
organic group having a carbon number of 2 to 17; $R^{2'}$ is,
when a plurality of $R^{2'}$ s are present, each is
independently, an aliphatic group having a carbon number
of 1 to 10, which may have a substituent; R^3 is, when a
plurality of R^3 s are present, each is independently, a
methyl group or an ethyl group; a is an integer of 1 or
2; b is an integer of 0, 1 or 2; and a+b is 3 or less},
at least one silanol compound represented by following
general formula (3):



{wherein each of R^4 and R^5 is an aliphatic,
alicyclic or aromatic group having a carbon number of 3
to 10, which may have a substituent} and a catalyst to
obtain a mixture, and polymerizing the mixture,

wherein the polyorganosiloxane contains a structure
represented by following general formula (2):



{wherein X is an organic group having a
carbon number of 1 to 15}, and

wherein from 5 to 60% by number of Si atoms in the
polyorganosiloxane are contained in the structure

represented by general formula (2).

[Claim 25]

5 The polyorganosiloxane according to claim 24,
wherein R^{1'} in general formula (I) is a group having an
acrylic acid ester and/or a methacrylic acid ester.