

DESCRIPTION

SILOXANE COMPOUND, CURABLE RESIN COMPOSITION, CURED PRODUCT
THEREOF AND OPTICAL SEMICONDUCTOR ELEMENT

Technical Field

[0001]

The present invention relates to a novel reactive functional group-containing siloxane compound, a method for producing the same and a composition thereof. More specifically, it relates to a curable resin composition for optical semiconductors being excellent in transparency, light fastness and low elastic modulus properties at a low temperature, and to an optical semiconductor element sealed with a cured product thereof.

Background Art

[0002]

As a sealing material for optical semiconductor elements such as LEDs, epoxy resins have been conventionally employed in terms of the balance of performance and economic efficiency. Bisphenol A-type epoxy resins, alicyclic epoxy resins and the like having an excellent balance of, particularly, heat resistance, transparency and mechanical properties have been widely used.

Recently, it is pointed out that progression of wavelength shortening (360 nm ~ 480 nm) of LED emission wavelength and improvement of luminescence intensity resulted in coloring of the above sealing material due to the effect of light and finally deterioration of the characteristics as LED.

So, silicone resins were under consideration for the purpose to avoid coloring of sealing material by light. However, silicone resins can be selected only in a sealed form of a gel state because of their inferior mechanical properties and adhesiveness compared with epoxy resins. The problem that tackiness and deformation of surfaces occur after sealing for the reason was pointed out in the market.

In order to improve fastness of the above epoxy resins and also tackiness properties of the above silicone resins, polyorganosiloxane having a weight average of 500 to 1000000 is obtained by heating a silane compound having an epoxy group and a silane compound having no epoxy group in the presence of an organic solvent, an organic base and water in Patent Literature 1. Said polyorganosiloxane is more improved than conventional epoxy resins in terms of light fastness. In addition, tackiness properties and hardness are improved by increasing the introduction amount of the trifunctional alkoxysilane compound relative to the bifunctional alkoxysilane compound. However, by hardening the cured product for improving surface tackiness properties and deformation, the elastic modulus particularly at a low-temperature region becomes higher (level of -30°C or less). As a result, reduction of low elastic modulus properties occur at a low temperature (-30°C or less) in heat cycle test.

It is one of the important properties in optical semiconductor sealants that sealant-cured products have a low elastic modulus at a low temperature, and improvement of this point is an important problem.

Related technical Literature

Patent Literature

[0003]

Patent Literature 1: WO 2005/100445 A1

Summary of the Invention

Problems to Be Solved by the Invention

[0004]

It is an object of the invention to provide a siloxane compound having a novel reactive functional group with both light fastness and low elastic modulus at a low temperature as an LED-sealing material, a curable resin composition using it, and an optical semiconductor element using said curable resin composition as a sealing

material.

Means of Solving the Problems

[0005]

The present inventors have intensively studied to solve the above problems and found that a reactive functional group-containing siloxane compound which has a chain silicone segment obtained by reaction of silicone oil (silicon compound) having a silanol terminal represented by the later-described general formula (2) with a reactive functional group-containing trialkoxysilane compound (silicon compound) containing an epoxy group and a hydrolysis condensation segment of trialkoxysilane is useful to solve the above-described problems. That is, they have found that a curable resin composition containing said siloxane compound satisfies the above problems. In addition, further, they have found that said siloxane compound can be efficiently synthesized by a 2-step reaction. In the result, the present invention has been completed.

In this regard, the siloxane compound of the present invention is, as indicated above, an oligomer (polymer) comprising a chain silicone segment and a hydrolysis condensation segment of alkoxysilane (preferably, silsesquioxane segment), and at least one of said hydrolysis condensation segments contains at least one reactive functional group having an epoxy group.

The present invention will be described below.

[0006]

That is, the present invention relates to:

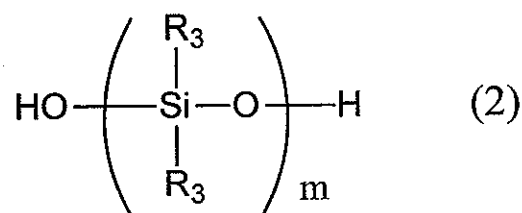
- (1) A reactive functional group-containing siloxane compound, which is a block-type siloxane oligomer having a chain silicone segment and a hydrolysis condensation segment of tri(C1-C10)alkoxysilane having a group selected from the group consisting of a reactive functional group having an epoxy group, a methyl group and a phenyl group, at least one of the hydrolysis condensation segments being a segment containing at least one reactive functional group having an epoxy

group,

(2) The reactive functional group-containing siloxane compound according to the above (1), wherein the hydrolysis condensation segment is a silsesquioxane segment,

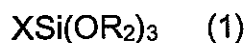
(3) The reactive functional group-containing siloxane compound according to Claim 1 or 2, which is obtained by, as a first step reaction, reacting silanol-terminal silicone oil (b) represented by the general formula (2):

[0007]



[0008]

(wherein, plural existing R_3 may be the same or different from each other and each represents a straight chain, branched or cyclic alkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 14 carbon atoms or an alkenyl group having 2 to 10 carbon atoms, and m represents 2 to 2000 as an average value) with an alkoxysilane compound (a) represented by the general formula (1):



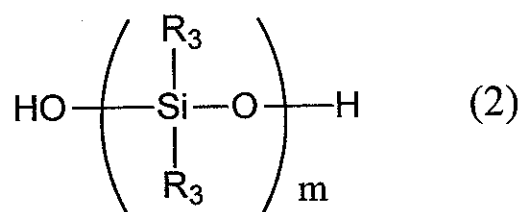
(wherein, X represents a reactive functional group having an epoxy group, and R_2 represents an alkyl group having 1 to 10 carbon atoms)

in the range that the alkoxy group equivalent of the alkoxysilane compound is 1.5 to 200 equivalents relative to 1 equivalent of the silanol group of the silanol-terminal silicone oil (b) for condensation, and then by, as a second step reaction, adding water to the resulting reaction liquid for hydrolysis condensation of the residual alkoxy group,

(4) The reactive functional group-containing siloxane compound according to Claim 3, wherein m is 2 to 200,

(5) The reactive functional group-containing siloxane compound according to the above (1), which is obtained by, as the first step reaction, reacting silanol-terminal silicone oil (b) represented by the general formula (2):

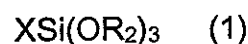
[0009]



[0010]

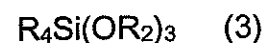
(wherein, plural existing R_3 may be the same or different from each other and each represents a straight chain, branched or cyclic alkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 14 carbon atoms or an alkenyl group having 2 to 10 carbon atoms, and m represents 2 to 200 as an average value)

with both an alkoxysilane compound (a) represented by the general formula (1):



(wherein, X represents a reactive functional group having an epoxy group and each R_2 represents an alkyl group having 1 to 10 carbon atoms)

and an alkoxysilane compound (c) represented by the general formula (3):



(wherein, R_4 represents a methyl group or a phenyl group, and R_2 may be the same or different from R_2 in the general formula (1) and each independently represents an alkyl group having 1 to 10 carbon atoms)

in the range that the total equivalent of the alkoxy group in the alkoxysilane compounds (a) and (c) is 1.5 to 200 equivalents relative to 1 equivalent of the silanol group in the silanol-terminal silicone oil (b) for condensation, and then by, as the second step reaction, adding water to the obtained a reaction liquid for hydrolysis·condensation of the residual alkoxy group,

(6) The reactive functional group-containing siloxane compound according to any

one of the above (3) to (5), wherein R_3 in the general formula (2) each independently represents a methyl group or a phenyl group, R_2 in the general formula (1) each independently represents a methyl group or an ethyl group, and R_2 in the general formula (3) may be the same or different from R_2 in the general formula (1) and each independently represents a methyl group or an ethyl group,

(7) The reactive functional group-containing siloxane compound according to any one of the above (3) to (6), wherein X in the general formula (1) is an epoxycyclohexyl ethyl group,

(8) The reactive functional group-containing siloxane compound according to any one of the above (3) to (6), wherein the weight average molecular weight (M_w) of the silanol-terminal silicone oil (b) of the general formula (2) is 300 to 18,000,

[0011]

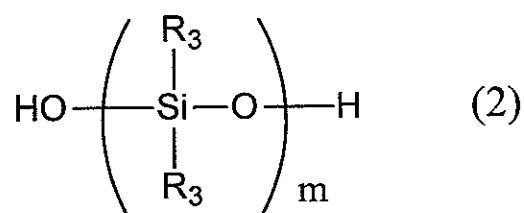
(9) The reactive functional group-containing siloxane compound according to any one of the above (1) to (8), wherein the weight average molecular weight (M_w) is 800 to 20,000,

(10) The reactive functional group-containing siloxane compound according to the above (1) or (2), which is characterized in that a substituent on the silicone in the chain silicone segment is any one or both of a methyl group or a phenyl group,

(11) The reactive functional group-containing siloxane compound according to the above (1) or (10), which is characterized in that the reactive functional group having an epoxy group in the silsesquioxane segment contains an epoxycyclohexyl group,

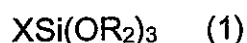
(12) A method for producing a reactive functional group-containing siloxane compound, which is characterized by, as a first step reaction, reacting silanol-terminal silicone oil (b) represented by the general formula (2):

[0012]



[0013]

(wherein, plural existing R_3 may be the same or different from each other and each independently represents a straight chain, branched or cyclic alkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 14 carbon atoms or an alkenyl group having 2 to 10 carbon atoms, and m represents 2 to 2000 as an average value) with an alkoxy silane compound (a) represented by the general formula (1):



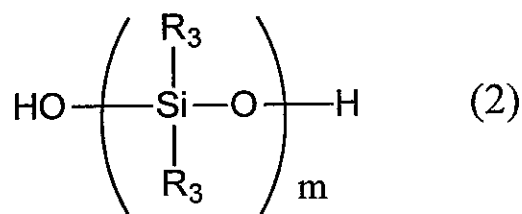
(wherein, X represents a reactive functional group having an epoxy group and R_2 represents an alkyl group having 1 to 10 carbon atoms)

in the range that the alkoxy group equivalent in the alkoxy silane compound (a) is 1.5 to 200 equivalents relative to 1 equivalent of the silanol group in the silanol-terminal silicone oil (b) and in the presence of a catalyst for condensation, and then by, as a second step reaction, adding water to the resulting reaction liquid for hydrolysis-condensation of the residual alkoxy group,

(13) The method for producing a reactive functional group-containing siloxane compound according to the above (12), wherein m is 2 to 200,

(14) A method for producing a reactive functional group-containing siloxane compound, which is characterized by, as a first step reaction, condensation reaction of silanol-terminal silicone oil (b) represented by the general formula (2):

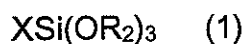
[0014]



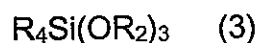
[0015]

(wherein, plural existing R_3 may be the same or different from each other and each independently represents a straight chain, branched or cyclic alkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 14 carbon atoms or an alkenyl group having 2 to 10 carbon atoms, and m represents 2 to 200 as an average value)

with an alkoxysilane compound (a) represented by the general formula (1):



(wherein, X represents a reactive functional group having an epoxy group and R_2 represents an alkyl group having 1 to 10 carbon atoms) and an alkoxysilane compound (c) represented by the following general formula (3):



(wherein, R_4 represents a methyl group or a phenyl group, and R_2 may be the same or different from R_2 in the general formula (1) and each independently represents an alkyl group having 1 to 10 carbon atoms)

in the range that the total equivalent of the alkoxy group in the alkoxysilane compounds (a) and (c) is 1.5 to 200 equivalents relative to 1 equivalent of the silanol group in the silanol-terminal silicone oil (b) and in the presence of a catalyst, and then by, as a second step reaction, adding water to the resulting reaction product for hydrolysis-condensation of the residual alkoxy group,

(15) The method for producing a reactive functional group-containing siloxane compound according to the above (12) to (14), which is characterized by successively conducting the first step reaction and the second step reaction in one-pot as a production process,

[0016]

(16) The method for producing a reactive functional group-containing siloxane compound according to the above (11) to (15), wherein the alkoxysilane compound represented by the general formula (1) is beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane or beta-(3,4-epoxycyclohexyl)ethyltriethoxysilane,

(17) The method for producing a reactive functional group-containing siloxane compound according to the above (12) to (16), wherein R_3 in the silanol-terminal silicone oil (b) represented by the general formula (2) may be the same or different from each other and each independently represents a methyl group or a phenyl group,

- (18) The method for producing a reactive functional group-containing siloxane compound according to the above (13) to (15), wherein the alkoxysilane compound represented by the general formula (3) is at least one kind selected from the group consisting of methyltrimethoxysilane, phenyltrimethoxysilane, methyltriethoxysilane and phenyltriethoxysilane,
- (19) A curable resin composition, which is characterized by containing the reactive functional group-containing siloxane compound (A) according to any one of the above (1) to (11) and a curing agent (B),
- (20) The curable resin composition according to the above (19), which is characterized by further containing a curing accelerator (C),
- (21) A cured product for optical semiconductors, which is obtained by heat curing the curable resin composition according to the above (19) or (20),
- (22) An optical semiconductor element, which is sealed with the cured product for optical semiconductors according to the above (20).

Effect of the Invention

[0017]

The cured product of the curable resin composition containing the siloxane compound of the present invention is free from tackiness properties and deformation and excellent in transparency, light fastness and low elastic modulus properties at a low temperature. Therefore, the curable resin composition of the present invention is extremely useful as a sealing material for optical semiconductors.

Mode for Carrying Out the Invention

[0018]

The reactive functional group-containing siloxane compound of the present invention (hereinafter also referred to as siloxane compound of the present invention, for simplicity) has, in 1 molecule, a chain silicone segment and a hydrolysis condensation segment of trialkoxysilane, preferably a silsesquioxane segment

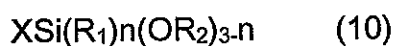
containing a reactive functional group having an epoxy group and more preferably a three-dimensional network silsesquioxane segment.

The siloxane compound of the present invention usually has a core of a hydrolysis condensation segment of trialkoxysilane, preferably a silsesquioxane segment of a network structure called silsesquioxane spreading in three dimensions, and a structure in which the chain silicone segment stretches and connects to a next hydrolysis condensation segment of trialkoxysilane, preferably a silsesquioxane segment. The present structure gives a balance of hardness and flexibility to the cured product of the curable composition of the present invention.

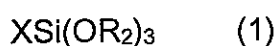
The siloxane compound of the present invention has a hydrolysis condensation segment of trialkoxysilane, preferably a silsesquioxane segment, and a chain silicone segment as described above, and in terms of that they are repeated, it can be a block-type siloxane compound.

[0019]

The siloxane compound of the present invention can be produced using, for example as a raw material, an alkoxysilane compound (a-1) (hereinafter also referred to as alkoxysilane (a-1)) represented by the following general formula (10):



(wherein, X represents a reactive functional group having an epoxy group, R_1 represents a substituted or unsubstituted alkyl group having 1 to 10 carbon atoms, a substituted or unsubstituted aryl group having 6 to 14 carbon atoms or a substituted or unsubstituted alkenyl group having 2 to 10 carbon atoms, R_2 represents alkyl group having 1 to 10 carbon atoms, n represents an integer number of 0 to 2, and when R_1 plurally exists, a plurality of R_1 may be the same or different from each other), preferably an alkoxysilane compound (a) (which is hereinafter also referred to as alkoxysilane (a)) represented by the following general formula (1):



(wherein, X and R_2 have the same meanings as in the above formula (10))

and silicone oil (b) represented by the general formula (2), and according to necessity,

an alkoxysilane compound (c) represented by the above general formula (3) can also be used as a raw material in combination with the above alkoxysilane (a-1), preferably (a). The chain silicone segment in the siloxane compound of the present invention is formed from silicone oil (b), and a hydrolysis condensation segment of trialkoxysilane, preferably a silsesquioxane segment and more preferably a three-dimensional network silsesquioxane segment, is formed from an alkoxysilane compound (a-1), preferably (a) {alkoxysilane (a-1), preferably (a), and alkoxysilane (c) when an alkoxysilane compound (c) (hereinafter also referred to as alkoxysilane (c)) is used in combination according to necessity}.

Said hydrolysis condensation segment is a segment formed in a 2-step reaction of hydrolysis and dealcoholization condensation of the alkoxy groups in preferably the above alkoxysilane (a) and according to necessity, (c). By said hydrolysis condensation, it has a configuration where a plurality of structural units as X (according to necessity, R₄) SiO_{3/2} are bonded. The siloxane compound formed from said structural unit is called silsesquioxane, whereby said hydrolysis condensation segment can be called silsesquioxane segment.

[0020]

Hereinafter, each raw material will be specifically explained.

X in the alkoxysilane compound (a-1) or (a) represented by the above general formula (10) or (1) is not particularly limited as long as it is an organic group having an epoxy group. It includes, for example, a glycidoxy C1-C4 alkyl group such as beta-glycidoxyethyl, gamma-glycidoxypropyl and gamma-glycidoxybutyl; a glycidyl group; an alkyl group having 1 to 5 carbon atoms substituted by a cycloalkyl group having 5 to 8 carbon atoms having an epoxy ring (oxirane ring), such as a beta-(3,4-epoxycyclohexyl)ethyl group, a gamma-(3,4-epoxycyclohexyl)propyl group, a beta-(3,4-epoxycycloheptyl)ethyl group, a beta-(3,4-epoxycyclohexyl)propyl group, a beta-(3,4-epoxycyclohexyl)butyl group and a beta-(3,4-epoxycyclohexyl)pentyl group. Among them, an alkyl group having 1 to 3 carbon atoms substituted by a glycidoxy group or an alkyl group having 1 to 3 carbon atoms substituted by a

cycloalkyl group having 5 to 8 carbon atoms having an epoxy ring, for example, a beta-glycidoxyethyl group, a gamma-glycidoxypropyl group or a beta-(3,4-epoxycyclohexyl)ethyl group is preferable, and a beta-(3,4-epoxycyclohexyl)ethyl group is particularly preferable.

[0021]

R_2 in the general formula (10) or (1) each independently represents an alkyl group having 1 to 10 carbon atoms and may be any of straight chain, branched or cyclic. It includes, for example, a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, an i-butyl group, a tert-butyl group, an n-pentyl group, an n-hexyl group, a cyclopentyl group, a cyclohexyl group and the like. For these R_2 , a methyl group or an ethyl group is preferable and a methyl group is particularly preferable, in terms of reaction conditions such as compatibility, reactivity and the like.

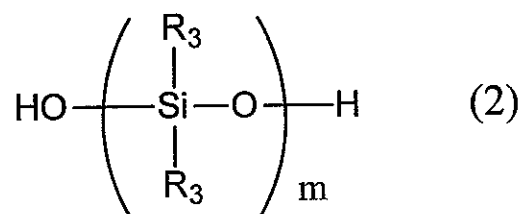
In addition, for R_1 in the general formula (10), the description of each group in the description of later-described R_3 in general formula (2) can be quoted as it is.

[0022]

Preferable specific examples of the alkoxysilane (a-1) or (a) represented by the general formula (10) or (1) include beta-glycidoxyethyltrimethoxysilane, beta-glycidoxyethyltriethoxysilane, gamma-glycidoxypropyltrimethoxysilane, gamma-glycidoxypropyltriethoxysilane, beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, beta-(3,4-epoxycyclohexyl)ethyltriethoxysilane and the like, and beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane is particularly preferable. These as the alkoxysilane compound (a) may be used alone or in combination of 2 or more kinds thereof, and can be also used in combination with later-mentioned alkoxysilane (c) represented by the general formula (3).

The silicone oil (b) is chain silicone oil having a silanol group at a terminal and having a structure represented by the following formula (2):

[0023]



[0024]

(wherein, R_3 and m are the same as described above).

In the general formula (2), plural existing R_3 may be the same or different from each other, and represents an alkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 14 carbon atoms or an alkenyl group having 2 to 10 carbon atoms.

The alkyl group having 1 to 10 carbon atoms can include a straight chain, branched or cyclic alkyl group having 1 to 10 carbon atoms, for example, a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, an i-butyl group, a sec-butyl group, a t-butyl group, an n-pentyl group, an i-pentyl group, an amyl group, an n-hexyl group, a cyclopentyl group, a cyclohexyl group, an octyl group, a 2-ethylhexyl group, a nonyl group, a decyl group and the like. Among them, a methyl group, an ethyl group or a cyclohexyl group is preferable, considering light fastness.

The aryl group having 6 to 14 carbon atoms can include, for example, a phenyl group, an o-tolyl group, an m-tolyl group, a p-tolyl group, a xylyl group and the like.

The alkenyl group having 2 to 10 carbon atoms can include an alkenyl group such as a vinyl group, a 1-methylvinyl group, an allyl group, a propenyl group, a butenyl group, a pentenyl group and a hexenyl group.

R_3 are preferably each independently a methyl group, a phenyl group, a cyclohexyl group or an n-propyl group in terms of light fastness and heat resistance and particularly preferably a methyl group or a phenyl group. Specifically, for the two R_3 in the general formula (2), the cases can be included that they are methyl or phenyl and that one is methyl and the other is phenyl. As for their combination, all the repeating units have usually the same combination thereof, while a different

combination may be mixed in the repeating units as long as effects of the present invention are achieved. For example, it may be different in each repeating unit, and in addition, a different combination thereof may be regularly or randomly mixed.

[0025]

m in the compound of the general formula (2) is, as an average value, 2 to 2000, preferably 2 to 200, more preferably 3 to 100 and particularly preferably 3 to 50. If m is too low, the cured product becomes so hard that low elastic modulus properties are reduced. If m is too high, the mechanical properties of the cured product tend to be deteriorated.

[0026]

The weight average molecular weight (Mw) of silicone oil (b) is usually within the range of 300 to 50,000, preferably within the range of 300 to 30,000 and further preferably in the range of 300 to 18,000 (GPC-measured value). Among them, the molecular weight is more preferably 300 to 10,000 considering the elastic modulus at a low temperature, further preferably 300 to 5,000 also considering the compatibility when composing, and particularly preferably 500 to 3,000.

If the weight average molecular weight is under 300, there is a possibility that the properties of the chain silicone segment moiety are hardly exhibited. For the molecular weight of the silicone oil (b) in the present invention, the weight average molecular weight (Mw) in terms of converting polystyrene was calculated by measuring under the below-described conditions using GPC (Gel Permeation Chromatography).

Conditions under GPC:

Manufacturer: Shimadzu Corporation;

Column: Guard column SHODEX GPC LF-G LF-804 (3 columns);

Flow rate: 1.0 ml/min.;

Column temperature: 40°C;

Solvent used: THF (tetrahydrofuran);

Detector: RI (differential refractive detector).

[0027]

The kinetic viscosity of the silicone oil (b) is preferably in the range of 10 to 200 cSt and more preferably 30 to 90 cSt. If the viscosity is too low, the viscosity of the intended siloxane compound of the present invention becomes low, resulting in that it may be not suitable as an optical semiconductor sealant, and if it is too high, the viscosity of the block-type siloxane compound (A) increases, resulting in that the workability tends to have harmful effects.

[0028]

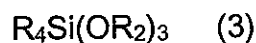
Specific examples of the silicone-terminal dimethyl silicone oil where R_3 in the silicone oil (b) are methyl groups can include the following product names. For example, it includes PRX413 and BY16-873 as the products from Toray Dow Corning Silicone Corporation, X-21-5841 and KF-9701 as the products from Shin-Etsu Chemical Co., Ltd., XC96-723, TSR160, YR3370, YF3800, XF3905, YF3057, YF3807, YF3802, YF3897 and XF3905 as the products from Momentive Performance Materials Inc., DMS-S12, DMS-S14, DMS-S15, DMS-S21, DMS-S27, DMS-S31, DMS-S32, DMS-S33, DMS-S35, DMS-S42, DMS-S45 and DMS-S51 as the products from Gelest, Inc., and the like. Preferable specific examples of the silicone-terminal methyl phenyl silicone oil where R_3 in the silicone oil (b) are a methyl group and a phenyl group can include the following product names. For example, it includes YF3804 as the products from Momentive Performance Materials Inc., PDS-0332 and PDS-1615 as the products from Gelest, Inc., and the like. As the silicone-terminal diphenyl silicone oil where R_3 in the silicone oil (b) are phenyl groups, specific examples of preferable product names can include, for example, PDS-9931 from Gelest, Inc. Among the above specific examples, PRX413, BY16-873, X-21-5841, KF-9701, XC96-723, YF3800, YF3804, DMS-S12, DMS-S14, DMS-S15, DMS-S21 and PDS-1615 are preferable in terms of molecular weight and kinetic viscosity. Among them, in order to give flexibility characteristics to the silicone segment, X-21-5841, XC96-723, YF3800, YF3804, DMS-S14 and PDS-1615 are particularly preferable in terms of molecular weight. These as the silicone oil (b)

may be used alone or in combination of 2 or more kinds thereof.

[0029]

Next, the alkoxysilane compound (c) will be specifically mentioned.

The alkoxysilane compound (c) has a structure of the following formula (3):



R_4 in the general formula (3) represents a methyl group or a phenyl group.

[0030]

R_2 in the general formula (3) may be the same or different from R_2 in the general formula (10) or (1), each independently represents an alkyl group having 1 to 10 carbon atoms, and may be any of straight chain, branched or cyclic. Specifically, it includes the same as those exemplified in the description of R_2 in the general formula (10) or (1) described above, including preferable groups and more preferably groups.

[0031]

Preferable specific examples of the alkoxysilane compound (c) include methyltrimethoxysilane, phenyltrimethoxysilane, methyltriethoxysilane, phenyltriethoxysilane and the like. Among the above, methyltrimethoxysilane or phenyltrimethoxysilane is preferable.

[0032]

In the present invention, the alkoxysilane compound (c) can be used in combination with an alkoxysilane compound (a-1), preferably (a), in order to control the molecular weight of block-type siloxane compound (A), the compatibility as a composition, the heat resistance, light fastness, low moisture permeability and low gas permeability of the cured product, and the like.

[0033]

The use amount of the alkoxysilane compound (c) is 0 to 70% by mol, preferably 0 to 55% by mol and more preferably 0 to 40% by mol relative to the total alkoxysilane compound (the total of (a-1), preferably (a), and (c)). When the alkoxysilane compound (c) is used in combination with the alkoxysilane compound (a), the alkoxysilane compound (c) is preferably used in the range of 5 to 70% by mol,

further preferably 5 to 50% by mol and particularly preferably 10 to 40% by mol relative to the total alkoxysilane compound.

[0034]

Hereinafter, the method for producing the siloxane compound of the present invention will be described.

The siloxane compound of the present invention can be, as the above, produced using an alkoxysilane compound (a-1) (hereinafter also referred to as alkoxysilane (a-1)), preferably an alkoxysilane compound (a) (hereinafter also referred to as alkoxysilane (a)), and the above silicone oil (b) as raw materials, and according to necessity, an alkoxysilane compound (c) can be used in combination as a raw material.

The production of the siloxane compound of the present invention can employ any methods as long as it can produce the siloxane compound of the present invention having the above two segments.

The most suitable method is the above method (one-pot method) where, as the first step reaction, silanol-terminal silicone oil (b) and alkoxysilane (a-1) preferably (a), and according to necessity, alkoxysilane (c) are reacted for condensation in the range that the alkoxy group equivalent of the above alkoxysilane compound is 1.5 to 200 equivalents relative to 1 equivalent of the silanol group in the silanol-terminal silicone oil (b), and then as the second step reaction, water is added to the resulting reaction liquid for hydrolysis condensation of the residual alkoxy group.

[0035]

The above first step reaction is preferably carried out in the absence of water and in the presence of an acid or base catalyst, preferably a base catalyst.

As for the ratio of the above alkoxysilane compound and the silicone oil (b) in the reaction of the alkoxysilane (a-1), preferably (a) (and according to necessity, an alkoxysilane (c) is used in combination) with the silicone oil (b) in the above first step reaction, the alkoxy group equivalent (which is, when an alkoxysilane (c) is used in combination, the total alkoxy equivalent in the alkoxysilane (a-1), preferably (a), and

the alkoxysilane (c)) in the alkoxysilane (a-1), preferably (a) (and according to necessity, an alkoxysilane (c) is used in combination) is usually 1.5 to 200 equivalents, preferably 2 to 200 equivalents, more preferably 2 to 150 equivalents and further preferably 2 to 100 equivalents relative to 1 equivalent of the silanol group in the silicone oil (b). In addition, as for said ratio, the alkoxy equivalent of the above alkoxysilane compound may be also 3 to 100 equivalents, preferably 4 to 100 equivalents and further preferably 5 to 100 equivalents relative to 1 equivalent of the silanol group in the silicone oil (b).

If the amount of the above alkoxysilane compound largely exceeds the above upper limit range, there is a possibility that the preferable physical properties of the obtained siloxane compound of the present invention are lost.

[0036]

In Patent Literature 1 (WO 2005/100445), silanol-terminal silicone oil (b) is not used and a silane compound having an epoxy group and a silane compound having no epoxy group are subjected to hydrolysis condensation in the presence of water at a time. For synthesis of silsesquioxane having a functional group, a method of hydrolysis condensation of an alkoxysilane compound having a functional group and an alkoxysilane compound having no functional group at a time in the presence of water is usually carried out likewise in Patent Literature 1.

However, when silicone oil (b) is used as a raw material in addition to alkoxysilane (a-1), preferably (a) (and alkoxysilane (c) according to necessity) as in the present invention, reaction of those raw materials altogether in the presence of a catalyst and water results in preferential progress of hydrolysis condensation reaction of the alkoxy groups in the alkoxysilane (a-1), preferably (a) (and alkoxysilane (c) according to necessity), whereby in some cases, a formed silsesquioxane compound and unreacted silicone oil (b) remain and these are incompatible, leading to a tendency of generating an inhomogeneous and white-turbid compound. Such white-turbid polyorganosiloxane is not suitable for optical application.

In addition, although the transparency is not affected, there are a tendency of reducing the molecular weight of the synthesized compound and also a possibility of reducing the heat resistance and generating "stickiness", whereby it is difficult to obtain a preferable siloxane compound of the present invention.

[0037]

The method for producing the reactive functional group-containing siloxane compound of the present invention including the above optimum method preferably goes through the production processes shown in the following (i) and (ii):

Production process (i): a process of forming an alkoxysilane modified form (d) by dealcoholization condensation of silanol-terminal silicone oil (b) and the above alkoxysilane for alkoxysilane modification of the silicone oil terminal (formation process of a chain silicone segment);

Production process (ii): a process of forming a hydrolysis condensation segment of alkoxysilane, preferably silsesquioxane segment, by hydrolysis condensation of the alkoxy groups in the alkoxysilane modified form (d) and the above alkoxysilane compound in the presence of water (formation process of a hydrolysis condensation segment of alkoxysilane).

In the production processes (i) and (ii), the reactions may be carried out in any order as long as going through each process.

In addition, in some cases, the reactions of the above production processes (i) and (ii) may be carried out in one process, where the silanol-terminal silicone oil (b) and the above alkoxysilane compound are reacted by such a method as sequentially adding water dropwise. Further, when silsesquioxane having 2 or more alkoxy substituents alternatively synthesized therefrom instead of the above alkoxysilane is used in (i), the siloxane compound of the present invention can be obtained only in the production process (i).

[0038]

Preferable production methods include, specifically, the following three kind production methods including the above optimum method.

<Production method (A)>

A method wherein:

Firstly, as the production process (i), a process of obtaining an alkoxysilane modified form (d) is carried out by dealcoholization condensation reaction of silicone oil (b) having a silanol group at the terminal with alkoxysilane (a) (and according to necessity, an alkoxysilane (c) may be used in combination) for modification of the silicone oil terminal to alkoxysilane.

Subsequently, as the production process (ii), the block-type siloxane compound of the present invention having a chain silicone segment {usually represented by $-(\text{OSi}(\text{R}_3)_2)_m-$ (wherein R_3 has the same meaning as in the formula (2))} and a hydrolysis condensation segment of alkoxysilane, preferably silsesquioxane segment, is produced by, preferably in the coexistence of alkoxysilane (a) (and according to necessity, an alkoxysilane (c) is used in combination), carrying out hydrolysis condensation reaction of the alkoxy groups in the alkoxysilane modified form (d) of silicone oil obtained in the production process (i) or, in the case of coexistence of the above alkoxysilane compound, the alkoxy groups in both the above alkoxysilane modified form (d) and the above alkoxysilane compound, in the presence of water.

<Production method (B)>

A method wherein:

Firstly, a process of obtaining hydrolysis condensate of alkoxysilane, preferably silsesquioxane (e), having an alkoxy group within the molecule is carried out by hydrolysis condensation reaction of the alkoxy groups in alkoxysilane (a) (and according to necessity, an alkoxysilane (c) is used in combination) in the presence of water.

Subsequently, the above siloxane compound of the present invention is produced by carrying out by preferably isolation of the hydrolysis condensate of alkoxysilane, preferably silsesquioxane (e), synthesized the above, , and then by dealcoholization condensation reaction of silicone oil (b) having a silanol group at the terminal and the hydrolysis condensate of alkoxysilane, preferably silsesquioxane (e),

obtained above, preferably in the absence of water.

<Production method (C)>

One-pot method wherein:

Firstly, as the production process (i), the above alkoxy silane modified form (d) is formed by dealcoholization condensation reaction of silicone oil (b) having a silanol group at the terminal with alkoxy silane (a) (and according to necessity, an alkoxy silane (c) is used in combination) preferably in the absence of water and in the presence of excessive alkoxy silane described above, and then as the production process (ii), the above siloxane compound of the present invention is produced by carrying out hydrolysis condensation reaction of the alkoxy groups in the residual alkoxy silane (a) (the residual alkoxy silane (a) and (c) in the case of using an alkoxy silane (c) in combination according to necessity) and in the above alkoxy silane modified form (d) in the presence of water.

[0039]

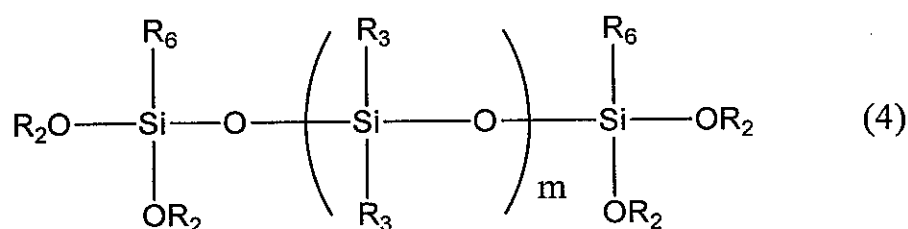
In the present invention, it is preferable in terms of shortening the production process to use the above-mentioned production method (C) of successive one-pot reaction where the second step reaction is directly carried out without isolation of the reactant in the first step.

Hereinafter, the production method (C) (the above most preferable production method) will be more specifically mentioned.

In the one-pot method, the production process (i) is the first step reaction and the production process (ii) is the second step reaction. Firstly, in the first step reaction (production process (i)), an alkoxy silane modified form (d) is obtained by carrying out dealcoholization condensation of silicone oil (b) and alkoxy silane (a) (and alkoxy silane (c) according to necessity) for modification of the hydrogen atom of the terminal silanol group in silicone oil (b) to alkoxy silyl. The first step reaction, which is carried out preferably without addition of water, does not cause hydrolysis condensation of the alkoxy groups, so it is considered that when the alkoxy group is reacted in an amount of 3 or more equivalents relative to 1 equivalent of the silanol

group, the alkoxy silane modified form (d) exists as a structure shown by the following formula (4), whereby it is considered preferable to carry out the subsequent hydrolysis condensation of the alkoxy groups after formation of such a modified form (d). Therefore, it is one of preferable aspects to carry out said reaction using 3 equivalents to 200 equivalents of the alkoxy group relative to 1 equivalent of the silanol group in the silicone oil (b).

[0040]



[0041]

In the formula (4), R_2 , R_3 and m have the same meanings as described above, and R_6 may be the same or different and each independently represents the above X and/or R_4 .

[0042]

In the first step reaction, if the alkoxy group is reacted in an amount of less than 1.0 equivalent relative to 1 equivalent of the silanol group, no alkoxy group exists at completion of the first step reaction resulting in no further progress to the second step reaction, while if the alkoxy group is reacted in an amount between 1.0 and 1.5 equivalents, 2 or more alkoxy groups in the alkoxy silane (a) (and alkoxy silane (c) according to necessity) are reacted with the silanol group in the silicone oil (b) resulting in a too high polymer molecule at completion of the first step reaction leading to gelation. Due to this, it is necessary to react the alkoxy group in an amount of 1.5 or more equivalents relative to 1 equivalent of the silanol group. In terms of reaction control, 2.0 or more equivalents are preferable.

In addition, it is preferable in terms of producing the hydrolysis condensation segment of alkoxy silane as a preferable silsesquioxane segment that the alkoxy group is used in an amount of 3 or more equivalents, preferably 4 or more equivalents

and further preferably 5 or more equivalents relative to 1 equivalent of the silanol group.

In this regard, the silsesquioxane segment in the present invention may be any of so-called general ladder-type, partially ring-opened cage-type or random-type structures, and it is considered to be usually a mixture thereof.

[0043]

After completion of the first step reaction, the second step reaction (production process (ii)) is carried out where water is added to the reaction liquid as it is for hydrolysis condensation of the alkoxy groups.

The addition amount of water is about 0.5 equivalent to 100 equivalents relative to 1 equivalent of the alkoxy group in the above alkoxysilane compound used as a raw material. Preferably, water is used in a volume of about 1 to 10 times, preferably about 1 to 5 times the theoretical amount of water necessary for hydrolysis condensation of the residual alkoxy group after completion of the first step reaction.

It is considered that the reactions (I) to (III) shown in the below-described occur in the second step reaction.

(I) Hydrolysis condensation reaction of the alkoxy groups of the residual alkoxysilane (a) (and alkoxysilane (c) when used in combination according to necessity) in the system.

(II) Hydrolysis condensation reaction of the alkoxy groups of the alkoxysilane modified form (d) obtained in the first step reaction and the alkoxysilane (a) (and alkoxysilane (c) when used in combination according to necessity).

(III) Condensation reaction of the alkoxy groups of the alkoxysilane modified form (d) obtained in the first step reaction and hydrolysis condensates of the alkoxysilane (a) (and alkoxysilane (c) when used in combination according to necessity) produced in the reaction of the above (I).

In the second step reaction, the above reactions simultaneously occur in combination, so formation of the above hydrolysis condensation segment, preferably silsesquioxane segment, and also condensation with the chain silicone segment from

the silicone oil (b) are carried out at a same time.

[0044]

The block-type siloxane compound of the present invention produced through the first step reaction and the second step reaction described above is excellent in transparency, and a cured body obtained from a resin composition using it is excellent in transparency and low elastic modulus properties.

[0045]

The production of the block-type siloxane compound having a reactive functional group of the present invention can be carried out without a catalyst, but using no catalyst will lead to delay of the reaction progress so it is preferable in terms of reduction in reaction time to carry out in the presence of a catalyst. A catalyst which can be used is any compound as long as it shows acidity or basicity. Examples of the acidic catalyst include inorganic acids such as hydrochloric acid, sulfuric acid and nitric acid and organic acids such as formic acid, acetic acid and oxalic acid. In addition, as for examples of the basic catalyst, alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, lithium hydroxide and cesium hydroxide, alkali metal carbonates such as sodium carbonate, potassium carbonate, sodium hydrogen carbonate and potassium hydrogen carbonate, inorganic bases such as ammonia, and organic bases such as triethylamine, diethylenetriamine, n-butylamine, dimethylaminoethanol, triethanolamine and tetramethyl ammonium hydroxide can be used. Among them, inorganic bases are preferable and particularly sodium hydroxide and potassium hydroxide are preferable, in terms of easiness of removing a catalyst from a product. The addition amount of the catalyst is usually 0.001 to 7.5% by weight and preferably 0.01 to 5% by weight relative to the total by weight of the alkoxysilane (a) (alkoxysilane (c) may be used in combination according to necessity) in the reaction system. Further, said addition amount may be about 0.01 to 1% by weight.

As for the method of adding the catalyst, the catalyst is directly added or used dissolved in a soluble solvent or the like. Above all, it is preferable to add the

catalyst in the state of being predissolved in an alcohol such as methanol, ethanol, propanol and butanol. In this case, its addition as an aqueous solution using water or the like promotes unilateral condensation of alkoxysilane (a) (according to necessity, alkoxysilane (c) used in combination) as described above, whereby there is a possibility that the produced silsesquioxane oligomer and silicone oil (b) are incompatible and white-turbid.

[0046]

The production of the reactive functional group-containing siloxane compound of the present invention can be carried out without or in a solvent. In addition, it is also possible to add a solvent in the middle of the production process. The solvent is preferably a solvent which dissolves alkoxysilane (a), silicone oil (b) (according to necessity, alkoxysilane (c) can be used in combination) and alkoxysilane modified form (d). Such a solvent can be exemplified by, for example, aprotic polar solvents such as dimethylformamide, dimethylacetamide and tetrahydrofuran, ketones such as methyl ethyl ketone, methylisobutylketone and cyclopentanone, esters such as ethyl acetate, butyl acetate, ethyl lactate and isopropyl butanoate, alcohols such as methanol, ethanol, propanol and butanol, hydrocarbons such as hexane, cyclohexane, toluene and xylene, and the like. In the present invention, the reaction is preferably in an alcohol and more preferably in methanol or/and ethanol, in terms of reaction control. The use amount of the solvent is not particularly limited as long as it is in the range that the reaction smoothly proceeds, and the solvent is usually used in an amount of about 0 to 900 parts by weight relative to the total weight 100 parts of alkoxysilane (a) (according to necessity, alkoxysilane (c) can be used in combination) and silicone oil (b). The reaction temperature depends on the catalyst amount but is usually 20 to 160°C, preferably 40 to 140°C and particularly preferably 50 to 150°C. In addition, the reaction time is usually 1 to 40 hours and preferably 5 to 30 hours, respectively in each production process.

[0047]

After completion of the reaction, the catalyst is removed by neutralization and/or

water washing, according to necessity. In the case of water washing, it is preferable to add a solvent which can be separated from water, depending on the kind of solvent. Preferable solvents can be exemplified by, for example, ketones such as methyl ethyl ketone, methylisobutylketone and cyclopentanone, esters such as ethyl acetate, butyl acetate, ethyl lactate and isopropyl butanoate, hydrocarbons such as hexane, cyclohexane, toluene and xylene, and the like.

[0048]

In the present reaction, the catalyst may be removed only by water washing, but the reaction is carried out under either acidic or basic condition so it is preferable that the water washing is carried out after neutralization or that the catalyst is absorbed using an absorbent and then the absorbent is removed by filtration. In the case of using an absorbent, an absorbent is added to the reaction liquid, treatments such as stirring and heating are carried out to absorb the catalyst, and then the catalyst and the absorbent can be removed by filtering the absorbent and also by washing the residue with water.

For the neutralization, a compound showing acidity or basicity can be used.

Examples of compounds showing acidity include inorganic acidic compounds such as hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid and sodium dihydrogenphosphate, or organic acids such as formic acid, acetic acid and oxalic acid. In addition, as for examples of compounds showing basicity, inorganic bases such as; alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, lithium hydroxide and cesium hydroxide; alkali metal carbonates such as sodium carbonate, potassium carbonate, sodium hydrogen carbonate and potassium hydrogen carbonate; and basic phosphates such as disodium hydrogenphosphate, trisodium phosphate, polyphosphoric acid and sodium tripolyphosphate; or organic bases such as ammonia, triethylamine, diethylenetriamine, n-butylamine, dimethylaminoethanol, triethanolamine, tetramethyl ammonium hydroxide and the like can be used. Among them, inorganic base or inorganic acid compounds are preferable in terms of easiness of removing from an intended product, and further

preferable are phosphates such as sodium dihydrogenphosphate or the above basic phosphates allowing easy adjustment of pH near to neutral.

[0049]

The absorbent can be exemplified by activated earth, activated carbon, zeolite, inorganic-organic synthetic absorbents, ion-exchange resin and the like, and specific examples thereof include products below.

The activated earth includes, for example, products from Toshin Chemicals Co., Ltd.: activated earth (SA35, SA1, T, R-15, or E) or Nikkanite (G-36, G-153 or G-168), products from Mizusawa Industrial Chemicals, Ltd.: Galleon Earth or Mizuka-Ace^{RTM} (the superscript RTM represents registered trademark, as is the same hereinafter), and the like.

The activated carbon includes, for example, products from Ajinomoto Fine-Techno Co., Inc.: CL-H, Y-10S or Y-10SF, products from Futamura Chemical Co., Ltd.: S, Y, FC, DP, SA1000, K, A, KA, M, CW130BR, CW130AR or GM130A, and the like.

The zeolite includes, for example, products from Union Showa K.K.: molecular sieve 3A, 4A, 5A or 13X, and the like.

The synthetic absorbent includes, for example, products from Kyowa Chemical Industry Co., Ltd.: Kyowardo^{RTM} 100, 200, 300, 400, 500, 600, 700, 1000 and 2000, products from Rohm and Haas Company: Amberlyst^{RTM} 15JWET, 15DRY, 16WET, 31WET, A21, Amberlite^{RTM} IRA400JCI, IRA403BLCI and IRA404JCI, products from Dow Chemical Company: Dowex^{RTM} 66, HCR-S, HCR-W2 or MAC-3, and the like.

[0050]

After completion of reaction or after neutralization, purification can be carried out by means of water washing, filtration and in addition, separation-purification commonly used. The purification means includes, for example, column chromatography, concentration under vacuum, distillation, extraction and the like. These purification means may be carried out alone or in combination of a plurality thereof.

[0051]

In the case of reaction using a water-mixable solvent as a reaction solvent, it is preferable that the water-mixable reaction solvent is removed from the system by distillation or concentration under vacuum after neutralization, and then water and a solvent which can be separated from water is added to the reaction system to dissolve an intended reaction product, whereafter water washing is carried out.

[0052]

After water washing, by removing the solvent used above by concentration under vacuum or the like, a reactive functional group-containing siloxane compound of the present invention can be obtained.

[0053]

The siloxane compound of the present invention is usually colorless and transparent in appearance and a liquid having flowability at 25°C.

The siloxane compound of the present invention obtained by the above reaction is a reactive functional group-containing block-type siloxane compound characterized in that it comprises a chain silicone segment as described above, preferably a chain silicone segment represented by $-(\text{Si}(\text{R}_3)_2\text{O})_m-$ (wherein, R_3 and m have the same meanings as in the above formula (2)), and a silsesquioxane segment represented by $(\text{R}_6\text{SiO}_{3/2})_{n_x}$ (wherein, R_6 is the same as in the above formula (4) and n_x represents 2 to 20 as an average value) as a constitutional unit and at least one of the silsesquioxane segments have at least one reactive functional group having an epoxy group.

In the silsesquioxane segment, as for the number of the reactive functional group having an epoxy group represented by X from the above alkoxysilane (a) relative to one silicon atom in the silsesquioxane segment, a ratio of 0.3 to 1 is preferable, further a ratio of 0.45 to 1 is more preferable, and a ratio of 0.6 to 1 is particularly preferable, on average. In addition, as for the group represented by R_4 from the above alkoxysilane (c) relative to one silicon atom in the silsesquioxane segment, a ratio of 0 to 0.7 is preferable, further a ratio of 0 to 0.55 is more preferable,

and a ratio of 0 to 0.4 is particularly preferable, on average.

[0054]

The preferable molecular weight of the siloxane compound of the present invention is, as a weight average molecular weight measured by GPC, about 500 to 20,000, more preferably about 800 to 20,000, further preferably about 1,000 to 10,000 and particularly preferably about 1,500 to 6,000. If the weight average molecular weight is too low, there is a possibility that the heat resistance is reduced, and if it is too high, the viscosity increases causing harmful effects on workability.

The weight average molecular weight is a weight average molecular weight (Mw) in terms of polystyrene measured using GPC (Gel Permeation Chromatography) under the below-described conditions.

Conditions for GPC:

Manufacturer: Shimadzu Corporation;

Column: Guard column, SHODEX GPC LF-G LF-804 (three columns);

Glow rate: 1.0 ml/min.;

Column temperature: 40°C;

Solvent used: THF (tetrahydrofuran);

Detector: RI (differential refractive detector).

[0055]

The epoxy equivalent of the siloxane compound of the present invention (measured in the method as described in JIS K-7236) is preferably 300 to 1,600 g/eq, more preferably 400 to 1,000 g/eq and particularly preferably 450 to 900 g/eq. If the epoxy equivalent is too small, the cured product becomes too hard and there is a possibility of less properties of low elastic modulus, and if it is too large, mechanical properties of the cured product are deteriorated.

[0056]

The viscosity of the siloxane compound of the present invention (measured by an E-type viscometer at 25°C) is usually about 50 to 20,000 mPa·s, preferably about 150 to 10,000 mPa·s, further preferably about 200 to 10,000 mPa·s and most

preferably about 200 to 5000 mPa·s. In addition, in some cases, it is more preferably 500 to 10,000 mPa·s and particularly it is further preferably 800 to 5,000 mPa·s.

[0057]

The ratio, relative to the total silicon atoms, of the silicon atom bonding to three oxygens belonging to the hydrolysis condensation segment of alkoxy silane, preferably a silsesquioxane segment, in the siloxane compound of the present invention may be about 5 to 95% by mol while it is preferably 5 to 50% by mol, more preferably 8 to 30% by mol and particularly preferably 10 to 25% by mol for sealing optical semiconductor elements. The rest is the ratio of the silicon atom belonging to the chain silicone segment. In this regard, the term "the total silicon atoms" described above means the total silicon atoms in the siloxane compound of the present invention. If the ratio, relative to the total silicon atoms, of the silicon atom bonding to three oxygens belonging to the silsesquioxane segment is below 5% by mol, the characteristics of the chain silicone segment appear too much, resulting in that when using as a component for a curable resin composition described later, a cured product of said resin composition tends to be too soft leading to a concern of surface tackiness and scratches. If it is over 50% by mol, the characteristics of the silsesquioxane segment appear too much, resulting in that when using as a component for the curable resin composition described later, a cured product of said resin composition is so hard that the low elastic modulus properties are reduced leading to a tendency of worse results of heat cycle test.

The siloxane compound of the present invention is characterized in that it has a chain silicone segment and a hydrolysis condensation segment of the above alkoxy silane (preferably silsesquioxane segment) as described above and that the latter segment has a reactive functional group having an epoxy group, and in particular it is also a significant characteristic that the siloxane compound of the present invention with a higher ratio of the chain silicone segment is suitable for optical semiconductor sealing. For example, as described above, the ratio of the

silicon atom belonging to the hydrolysis condensation segment of the above alkoxy silane (preferably silsesquioxane segment) relative to the total silicon atoms in the siloxane compound of the present invention is 5 to 50% by mol, the ratio of the silicon atom belonging to the chain silicone segment is 50 to 95% by mol. In addition, a preferable ratio of the silicon atom belonging to the chain silicone segment is 70 to 92% by mol and further preferable is 75 to 90% by mol.

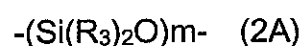
The ratio of the silicon atom in the two segments in the siloxane compound of the present invention may be calculated from the addition ratio of a raw material or can be also determined by ^1H NMR, ^{29}Si NMR, elemental analysis and the like of an obtained siloxane compound of the present invention.

[0058]

The siloxane compound of the present invention is summarized as described below:

(i) A reactive functional group-containing siloxane compound which is a block-type siloxane oligomer having a chain silicone segment and a hydrolysis condensation segment of tri(C1-C10)alkoxy silane having a group selected from the group consisting of a reactive functional group having an epoxy group, a methyl group and a phenyl group, and at least one of the hydrolysis condensation segments being a segment containing at least one reactive functional group having an epoxy group.

(ii) The reactive functional group-containing siloxane compound according to the above (i), wherein the chain silicone segment is a segment represented by the following formula (2A):



(wherein, R_3 may be the same or different from each other and represents a straight chain, branched or cyclic alkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 14 carbon atoms or an alkenyl group having 2 to 10 carbon atoms, and m represents 2 to 2000 as an average value).

(iii) The reactive functional group-containing siloxane compound according to the above (ii), wherein R_3 is an alkyl group having 1 to 10 carbon atoms and m is 2 to 200

on average.

(iv) The reactive functional group-containing siloxane compound according to any one of the above (i) to (iii), wherein R_3 is a methyl group.

[0059]

(v) The reactive functional group-containing siloxane compound according to any one of the above (i) to (iv), wherein the reactive functional group having an epoxy group is an alkyl group having 1 to 3 carbon atoms substituted by a cycloalkyl group having 5 to 8 carbon atoms having an epoxy group.

(vi) The reactive functional group-containing siloxane compound according to any one of the above (i) to (iv), wherein the tri(C1-C10)alkoxysilane having a group selected from the group consisting of a reactive functional group having an epoxy group, a methyl group and a phenyl group is tri(C1-C10)alkoxysilane having an alkyl group of 1 to 3 carbon atoms substituted by a cycloalkyl group of 5 to 8 carbon atoms having an epoxy group.

(vii) The reactive functional group-containing siloxane compound according to the above (vi), wherein the tri(C1-C10)alkoxysilane having an alkyl group of 1 to 3 carbon atoms substituted by a cycloalkyl group of 5 to 8 carbon atoms having an epoxy group is beta-(3,4 epoxycyclohexyl)ethyltrimethoxysilane.

(viii) The reactive functional group-containing siloxane compound according to any one of the above (i) to (vii), wherein the tri(C1-C10)alkoxysilane having a group selected from the group consisting of a reactive functional group having an epoxy group, a methyl group and a phenyl group is both tri(C1-C10)alkoxysilane having a reactive functional group having an epoxy group and tri(C1-C10)alkoxysilane having a group selected from the group consisting of a methyl group and a phenyl group.

(ix) The reactive functional group-containing siloxane compound according to the above (viii), wherein the tri(C1-C10)alkoxysilane having a group selected from the group consisting of a methyl group and a phenyl group is phenyltrimethoxysilane or methyltrimethoxysilane.

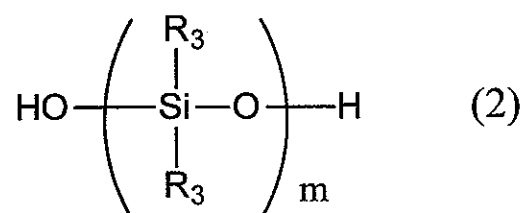
(x) The reactive functional group-containing siloxane compound according to any

one of the above (i) to (ix), wherein the weight average molecular weight measured by GPC is 500 to 20,000.

[0060]

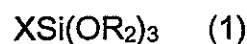
(xi) The reactive functional group-containing siloxane compound according to any one of the above (i) to (x), which is obtained by, as a first step reaction, reacting silanol-terminal silicone oil (b) represented by the general formula (2):

[0061]



[0062]

(wherein, plural existing R_3 may be the same or different from each other and each represents a straight chain, branched or cyclic alkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 14 carbon atoms or an alkenyl group having 2 to 10 carbon atoms, and m represents 2 to 2000 as an average value) with an alkoxysilane compound (a) represented by the general formula (1):



(wherein, X represents a reactive functional group having an epoxy group, and R_2 represents an alkyl group having 1 to 10 carbon atoms)

in the range that the alkoxy group equivalent of the alkoxysilane compound is 1.5 to 200 equivalents relative to 1 equivalent of the silanol group of the silanol-terminal silicone oil (b) for condensation, and then by, as a second step reaction, adding water to the resulting reaction liquid for hydrolysis-condensation of the residual alkoxy group.

[0063]

(xii) The reactive functional group-containing siloxane compound according to the above (xi), wherein the weight average molecular weight measured by GPC (Gel Permeation Chromatography) of the silanol-terminal silicone oil (b) represented by

the general formula (2) is 300 to 30,000.

(xiii) The reactive functional group-containing siloxane compound according to the above (xi) or (xii), wherein the equivalent of the alkoxy group in the alkoxysilane compound (a) represented by the general formula (1) is 2 to 100 equivalents relative to 1 equivalent of the silanol group in the silanol-terminal silicone oil (b).

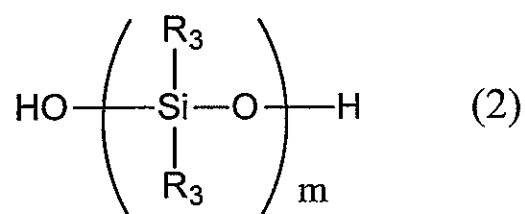
(xiv) The reactive functional group-containing siloxane compound according to any one of (xi) to (xiii), wherein the silanol-terminal silicone oil (b) represented by the general formula (2) is silanol-terminal dimethyl silicone oil or silanol-terminal methyl phenyl silicone oil.

(xv) The reactive functional group-containing siloxane compound according to any one of (xi) to (xiv), wherein the alkoxysilane compound (a) represented by the general formula (1) is beta-glycidoxyethyltrimethoxysilane, beta-glycidoxyethyltriethoxysilane, gamma-glycidoxypropyltrimethoxysilane, gamma-glycidoxypropyltriethoxysilane, beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane or beta-(3,4-epoxycyclohexyl)ethyltriethoxysilane.

[0064]

(xvi) The reactive functional group-containing siloxane compound according to any one of the above (i) to (x), which is obtained by, as a first step reaction, reacting silanol-terminal silicone oil (b) represented by the general formula (2):

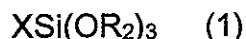
[0065]



[0066]

(wherein, plural existing R₃ may be the same or different from each other and each represents a straight chain, branched or cyclic alkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 14 carbon atoms or an alkenyl group having 2 to 10 carbon atoms, and m represents 2 to 200 as an average value)

with both an alkoxysilane compound (a) represented by the general formula (1):



(wherein, X represents a reactive functional group having an epoxy group and R₂ represents an alkyl group having 1 to 10 carbon atoms) and an alkoxysilane compound (c) represented by the general formula (3):



(wherein, R₄ represents a methyl group or a phenyl group, and R₂ may be the same or different from R₂ in the general formula (1) and each independently represents an alkyl group having 1 to 10 carbon atoms)

in the range that the total equivalent of the alkoxy group in the alkoxysilane compounds (a) and (c) is 1.5 to 200 equivalents relative to 1 equivalent of the silanol group in the silanol-terminal silicone oil (b) for condensation, and then by, as a second step reaction, adding water to the obtained reaction liquid for hydrolysis-condensation of the residual alkoxy group.

(xvii) The reactive functional group-containing siloxane compound according to the above (xvi), wherein the silanol-terminal silicone oil (b) represented by the general formula (2) is the silicone oil according to the above (xii) or (xiv).

(xviii) The reactive functional group-containing siloxane compound according to the above (xvi) or (xvii), wherein the alkoxysilane compound (a) represented by the general formula (1) is the compound according to the above (xv).

(xix) The reactive functional group-containing siloxane compound according to any one of the above (xvi) to (xviii), wherein the alkoxysilane compound (c) represented by the general formula (3) is methyltrimethoxysilane or phenyltrimethoxysilane.

[0067]

Next, the curable resin composition of the present invention will be explained.

The siloxane compound of the present invention can be used as a component for a curable resin composition. Hereinafter, the siloxane compound of the present invention is referred to as "siloxane compound (A) of the present invention" or simply "siloxane compound (A)" in explanation of said curable resin composition. In this

case, the siloxane compound (A) may be the reactive functional group-containing siloxane compound according to any one of the above (i) to (xix) and includes all combinations with said siloxane compound.

The curable resin composition of the present invention contains the siloxane compound (A) of the present invention as an epoxy resin component and further contains a curing agent (B). In addition, according to necessity, it may further contain another epoxy resin other than the siloxane compound (A) or/and a curing accelerator (C). Said other epoxy resin can be used in combination within the range that the properties of the siloxane compound (A) of the present invention, for example, the properties as a cured product when used in a curable resin composition, specifically transparency, heat resistance, light fastness, low elastic modulus properties at a low temperature, non-tackiness properties, heat cycle resistance, hardness and the like are not lost. In some cases, said other epoxy resin improves physical properties of cured products of the curable resin composition. The ratio of the siloxane compound (A) of the present invention relative to the whole epoxy resin component is 20 to 100% by weight, preferably 30 to 100% by weight and further preferably 50 to 100% by weight and it may be 60 to 100% by weight or 70 to 100% by weight and also 80 to 100% by weight, depending on the use aspect.

When used in combination, the ratio of the siloxane compound of the present invention in the whole epoxy resin of the siloxane compound (A) of the present invention together with another epoxy resin is preferably 20 to 90% by weight and particularly preferably 30 to 90% by weight.

Further, in the curable resin composition of the present invention, the ratio of the siloxane compound (A) of the present invention alone or the whole epoxy resin of the siloxane compound (A) of the present invention together with another epoxy resin is about 30 to 90% by weight, more preferably 40 to 90% by weight and preferably about 50 to 90% by weight relative to the whole said composition. Also, it is 40 to 80% by weight and preferably about 50 to 80% by weight, depending on the embodiment.

Specific examples of other epoxy resins include polyfunctional epoxy resins as a glycidyl-etherified product of a polyphenol compound, polyfunctional epoxy resins as a glycidyl-etherified product of various novolak resins, nuclearly hydrogenated products of aromatic epoxy resins, alicyclic epoxy resins, heterocyclic epoxy resins, glycidyl ester-type epoxy resins, glycidyl amine-type epoxy resins, epoxy resins in which a halogenated phenol is glycidylated, glycidylated silicone resin or the like.

[0068]

The polyphenol compound used in the above polyfunctional epoxy resin can include bisphenol A, bisphenol F, bisphenol S, 4,4'-biphenol, tetramethyl bisphenol A, dimethyl bisphenol A, tetramethyl bisphenol F, dimethyl bisphenol F, tetramethyl bisphenol S, dimethyl bisphenol S, tetramethyl-4,4'-biphenol, dimethyl-4,4'-biphenylphenol, 1-(4-hydroxyphenyl)-2-[4-(1,1-bis-(4-hydroxyphenyl)ethyl)phenyl]propane, 2,2'-methylene-bis(4-methyl-6-tert-butylphenol), 4,4'-butylidene bis(3-methyl-6-tert-butylphenol), trishydroxyphenylmethane, resorcinol, hydroquinone, pyrogallol, phenols having a diisopropylidene skeleton, phenols having a fluorene structure such as 1,1-di-4-hydroxyphenyl fluorene, and polyphenol compounds such as phenolated polybutadiene. Therefore, the polyfunctional epoxy resin as the above glycidyl-etherified product of a polyphenol compound can specifically include glycidyl-etherified products of the above polyphenol compounds.

The novolak resin used in the above polyfunctional epoxy resin can include novolak resins from various phenols as a raw material, including various novolak resins such as novolak resin from various phenols, for example, phenol, cresols, ethylphenols, butylphenols, octylphenols, bisphenol A, bisphenol F, bisphenol S and naphthols as a raw material, xylene skeleton-containing phenol novolak resin, dicyclopentadiene skeleton-containing phenol novolak resin, biphenyl skeleton-containing phenol novolak resin and fluorene skeleton-containing phenol novolak resin. Therefore, the polyfunctional epoxy resin as the glycidyl-etherified product from various novolak resins specifically includes glycidyl-etherified products

of these novolak resins.

[0069]

The nuclearily hydrogenated products of the aromatic epoxy resins include nuclearily hydrogenated products of glycidyl-etherified products of a novolak resin in which a novolak resin from the above various phenols as a raw material is a raw material, and specifically include nuclearily hydrogenated products of glycidyl-etherified products of a novolak resin from various phenols, for example, a phenol compound such as bisphenol A, bisphenol F, bisphenol S and 4,4'-biphenol or glycidyl-etherified products of a novolak resin from phenol, cresols, ethylphenols, butylphenols, octylphenols, bisphenol A, bisphenol F, bisphenol S and naphthols, and the like as a raw material.

The alicyclic epoxy resins can include alicyclic epoxy resins having an aliphatic skeleton such as cyclohexane, which include 2,2'-bis(4-glycidyloxycyclohexyl)propane, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, vinylcyclohexene dioxide, 2-(3,4-epoxycyclohexyl)-5,5-spiro-(3,4-epoxycyclohexane)-1,3-dioxane, bis(3,4-epoxycyclohexyl)adipate and the like.

The aliphatic-type epoxy resins can include glycidyl ethers of polyhydric alcohol, for example, glycidyl ethers of polyhydric alcohol such as 1,4-butanediol, 1,6-hexanediol, polyethylene glycol, polypropylene glycol, pentaerythritol and xylylene glycol derivatives.

The heterocyclic epoxy resins can include heterocyclic epoxy resins having a heterocyclic ring such as isocyanuric ring and hydantoin ring, and the like.

The glycidyl ester-type epoxy resins can include epoxy resins made from glycidyl esters of carboxylic acid such as hexahydrophthalic acid diglycidyl ester and tetrahydrophthalic acid diglycidyl ester, and the like.

The glycidyl amine-type epoxy resins can include epoxy resins in which an amine, such as aniline, toluidine, p-phenylene diamine, m-phenylene diamine, diaminodiphenylmethane derivatives and diaminomethylbenzene derivatives, and the

like is glycidylated.

The epoxy resins in which a halogenated phenol is glycidylated include epoxy resins in which a halogenated phenol, such as brominated bisphenol A, brominated bisphenol F, brominated bisphenol S, brominated phenol novolak, brominated cresol novolak, chlorinated bisphenol S and chlorinated bisphenol A is glycidylated.

[0070]

In use of these epoxy resins, there is no particular limitation, but one having less colorability is more preferable in terms of transparency. Usually, a polyfunctional epoxy resin as a glycidylated product of bisphenol A, bisphenol F, bisphenol S, 4,4'-biphenol, tetramethyl-4,4'-biphenol, 1-(4-hydroxyphenyl)-2-[4-(1,1-bis-(4-hydroxyphenyl)ethyl)phenyl]propane, trishydroxyphenylmethane, resorcinol, 2,6-ditert-butylhydroquinone, phenols having a diisopropylidene skeleton, or phenols having a fluorene skeleton such as 1,1-di-4-hydroxyphenyl fluorene; a glycidyl-etherified product of various novolak resins such as novolak resin from various phenols such as phenol, cresols, bisphenol A, bisphenol S and naphthols as a raw material, dicyclopentadiene skeleton-containing phenol novolak resin, biphenyl skeleton-containing phenol novolak resin and fluorene skeleton-containing phenol novolak resin; a nuclearly hydrogenated product of a glycidyl-etherified product of a phenol compound such as bisphenol A, bisphenol F, bisphenol S and 4,4'-biphenol, or of a glycidyl-etherified product of a novolak resin from various phenols such as phenol, cresols, ethylphenols, butylphenols, octylphenols, bisphenol A, bisphenol F, bisphenol S and naphthols as a raw material; an alicyclic epoxy resin having a cyclohexane skeleton such as 3,4-epoxycyclohexylmethyl 3',4'-cyclohexylcarboxylate; glycidyl ethers of 1,6-hexanediol, polyethylene glycol and polypropylene glycol; triglycidyl isocyanurate or hexahydrophthalic acid diglycidyl ester; or the like is preferably used, and an alicyclic epoxy resin having a cyclohexane skeleton are particularly preferable in terms of heat-resistant transparency and light resistant transparency. These epoxy resins can be used in combination as a mixture of 1 kind or 2 or more kinds according

to necessity of imparting heat resistance and the like.

[0071]

The curing agent (B) and the curing accelerator (C) used in the present invention will be specifically described.

As the curing agent (B), an amine-type compound, an acid anhydride-type compound, a carboxylic acid-type compound, an amide-type compound, a phenol-type compound or the like can be used without any particular limitation. Specifically, it includes diaminodiphenylmethane, diethylenetriamine, triethylenetetramine, diaminodiphenylsulfone, isophoronediamine, dicyandiamide, tetraethylenepentamine, dimethylbenzylamine, ketimine compounds, polyamide resin synthesized from a dimer of linolenic acid and ethylenediamine, phthalic acid anhydride, trimellitic acid anhydride, pyromellitic acid anhydride, maleic acid anhydride, tetrahydrophthalic acid anhydride, methyltetrahydrophthalic acid anhydride, hydrogenated nadic acid anhydride, hydrogenated methylnadidic acid anhydride, methylnadidic acid anhydride, hexahydrophthalic acid anhydride, methylhexahydrophthalic acid anhydride, 1,3,4-cyclohexanetricarboxylic acid-3,4-anhydride, phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, methylhexahydrophthalic acid, trimellitic acid, cyclohexanetricarboxylic acid, 1,2,3,4-butanetetracarboxylic acid, bisphenols, polycondensate of phenols (such as phenol, alkyl-substituted phenol, naphthol, alkyl-substituted naphthol, dihydroxybenzene, dihydroxynaphthalene) and various aldehydes, polymerization products of a phenols and various diene compounds, polycondensates of phenols and aromatic dimethylol, or condensates of bismethoxymethylbiphenyl and naphthols or phenols, biphenols and modified products thereof, imidazole, boron trifluoride-amine complexes, guanidine derivatives, and the like. Among them, acid anhydride-type compounds and carboxylic acid-type compounds are particularly preferable, and hexahydrophthalic acid anhydride, methylhexahydrophthalic acid anhydride, 1,3,4-cyclohexanetricarboxylic acid-3,4-anhydride, hydrogenated nadic acid anhydride and hydrogenated methylnadidic acid anhydride are particularly

preferable, in terms of proper work life of the resin composition produced by mixing with an epoxy resin and transparency of the cured product.

The use amount of the curing agent (B) is preferably about 0.2 to 1.5 equivalents and particularly preferably about 0.3 to 1.2 equivalents, relative to 1 equivalent of an epoxy group in the total epoxy resin of the siloxane compound (A), together with another epoxy resin in the composition. In addition, the use amount of the curing agent particularly when using tertiary amine such as benzyl dimethylamine as the curing agent (B) is preferably 0.3 to 20% by weight and particularly preferably 0.5 to 10% by weight, relative to the epoxy group-containing compound in the composition.

[0072]

The curing accelerator (C) includes, for example, various imidazoles such as 2-methylimidazole, 2-phenylimidazole, 2-undecyl imidazole, 2-heptadecyl imidazole, 2-phenyl-4-methylimidazole, 1-benzyl-2-phenylimidazole, 1-benzyl-2-methylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-phenylimidazole, 1-cyanoethyl-2-undecylimidazole, 2,4-diamino-6(2'-methylimidazole(1'))ethyl-s-triazine, 2,4-diamino-6(2'-undecylimidazole(1'))ethyl-s-triazine, 2,4-diamino-6(2'-ethyl, 4-methylimidazole(1'))ethyl-s-triazine, 2,4-diamino-6(2'-methylimidazole(1'))ethyl-s-triazine · isocyanuric acid adduct, 2:3 adduct of 2-methylimidazole isocyanuric acid, 2-phenylimidazole isocyanuric acid adduct, 2-phenyl-3,5-dihydroxymethylimidazole, 2-phenyl-4-hydroxymethyl-5-methylimidazole, 1-cyanoethyl-2-phenyl-3,5-dicyanoethoxymethylimidazole; and salts of those imidazoles and polycarboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, pyromellitic acid, naphthalene dicarboxylic acid, maleic acid and oxalic acid; amides such as dicyandiamide; diaza compounds such as 1,8-diaza-bicyclo(5.4.0)undecene-7; and salts thereof, such as tetraphenylborate and phenol novolak; salts with the above polycarboxylic acids or phosphinic acids;

ammonium salts such as tetrabutylammonium bromide, cetyltrimethylammonium bromide, cetyltrimethylammonium hydroxide and trioctylmethylammonium bromide; phosphines and phosphonium compounds such as triphenylphosphine, tri(tolyl)phosphine, tetraphenylphosphonium bromide, tetraphenylphosphonium tetraphenylborate and methyltributylphosphonium dimethylphosphate; phenols such as 2,4,6-trisaminomethylphenol; and amine adducts. For example, commercial products thereof include U-CAT 18X (which is a trade name: manufactured by San-Apro Ltd.) and the like. These curing accelerators may be microencapsulated. These curing accelerators are appropriately selected according to the properties which are required for transparent resin compositions, for example, transparency, curing rate and working conditions. The curing accelerator is used in an amount ranging usually 0.001 to 15 parts by weight and preferably 0.005 to 5 parts by weight, and further preferably 0.05 to 1 parts by weight, relative to 100 parts by weight of the block-type siloxane compound (A) having a reactive functional group, or together with another epoxy resin.

[0073]

To the curable resin composition of the present invention, an inorganic filler, a colorant, a silicone resin, a leveling agent, a lubricant, a coupling agent, a leveling agent, a lubricant, a light stabilizer, an antioxidant, a phosphor and the like can be appropriately added according to a purpose, in the range that the transparency is not impaired.

The inorganic filler is not particularly limited and includes crystalline or amorphous silica, talc, silicon nitride, boron nitride, alumina, silica-titania mixed-melt and the like.

The colorant is not particularly limited and includes organic-type coloring matters of phthalocyanine, azo, disazo, quinacridone, anthraquinone, flavanthrone, perinone, perylene, dioxazine, condensed azo and azomethine-types, and inorganic pigments such as titanium oxide, lead sulfate, chrome yellow, zinc yellow, chrome vermillion, red oxide, cobalt violet, iron blue, ultramarine blue, carbon black, chrome

green, oxidation chrome and cobalt green.

The silicone resin includes dimethyl silicone, phenylmethyl silicone, epoxy-modified silicone, polyether-modified silicone, amine-modified silicone, vinyl-modified silicone, silyl-modified silicone and the like.

[0074]

The leveling agent includes oligomers having a molecular weight of 4,000 to 12,000 and comprising an acrylate such as ethyl acrylate, butyl acrylate and 2-ethylhexyl acrylate, epoxidized soybean fatty acid, epoxidized abietyl alcohol, hydrogenated castor oil, titanium-type coupling agents and the like.

[0075]

The lubricant includes hydrocarbon-type lubricants such as paraffin wax, microcrystalline wax and polyethylene wax; higher fatty acid-type lubricants such as lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid and behenic acid; higher fatty acid amide-type lubricants such as stearylamine, palmitylamine, oleylamine, methylenebisstearamide and ethylenebisstearamide; higher fatty acid ester-type lubricants such as hydrogenated castor oil, butyl stearate, ethylene glycol mono stearate, penta erythritol (mono-, di-, tri-, or tetra-)stearate; alcohol-type lubricants such as cetyl alcohol, stearyl alcohol, polyethylene glycol and polyglycerol; metal soaps as salts of lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, ricinoleic acid, naphthenic acid and the like with metals such as magnesium, calcium, cadmium, barium, zinc and lead; and natural waxes such as carnauba wax, candelilla wax, bees wax and montan wax.

[0076]

The coupling agent includes silane-type coupling agents such as 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, N-(2-aminoethyl)3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl)3-aminopropylmethyltrimethoxysilane, 3-aminopropyltriethoxysilane,

3-mercaptopropyltrimethoxysilane, vinyltrimethoxysilane, N-(2-(vinylbenzylamino)ethyl)3-aminopropyltrimethoxysilane hydrochloride, 3-methacryloxypropyltrimethoxysilane, 3-chloropropylmethyldimethoxysilane and 3-chloro propyl trimethoxysilane; titanium-type coupling agents such as isopropyl (N-ethylaminoethyl amino)titanate, isopropyltriisostearoyltitanate, titanium di(dioctylpyrophosphate)oxyacetate, tetraisopropyl di(dioctylphosphite)titanate and neoalkoxy tri(p-N-(beta-aminoethyl)aminophenyl)titanate; zirconium-type or aluminum-type coupling agents such as Zr-acetylacetonate, Zr-methacrylate, Zr-propionate, neoalkoxy zirconate, neoalkoxy trisneodecanoyl zirconate, neoalkoxy tris(dodecanoyl)benzenesulfonyl zirconate, neoalkoxy tris(ethylenediaminoethyl)zirconate, neoalkoxy tris(m-aminophenyl)zirconate, ammonium zirconium carbonate, Al-acetylacetonate, Al-methacrylate and Al-propionate.

[0077]

As the light stabilizer, a hindered amine-type light stabilizer (HALS) is suitable. The HALS is not particularly limited but typical ones include polycondensate of dibutylamine and 1,3,5-triazine, N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-1,6-hexamethylenediamine and N-(2,2,6,6-tetramethyl-4-piperidyl)butylamine, succinic acid dimethyl-1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine polycondensate, poly[{6-(1,1,3,3-tetramethylbutyl)amino-1,3,5-triazine-2,4-diyl}[(2,2,6,6-tetramethyl-4-piperidyl)imino]hexamethylene[(2,2,6,6-tetramethyl-4-piperidyl)imino]}, bis(1,2,2,6,6-pentamethyl-4-piperidyl)[[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]methyl]butylmalonate, bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate, 2-(3,5-di-t-butyl-4-hydroxybenzyl)-2-n-butylmalonic acid bis(1,2,2,6,6-pentamethyl-4-piperidyl) and the like. HALSs may be used alone or in combination of 2 or more kinds.

[0078]

The antioxidant includes phenol-type, sulfur-type and phosphorus-type antioxidants.

Specific examples of the phenol-type antioxidant are exemplified by monophenols such as 2,6-di-*t*-butyl-*p*-cresol, butylated hydroxyanisole, 2,6-di-*t*-butyl-*p*-ethylphenol, stearyl-beta-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate, isooctyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate, 2,4-bis-(*n*-octylthio)-6-(4-hydroxy-3,5-di-*t*-butylanilino)-1,3,5-triazine, and 2,4-bis[(octylthio)methyl]-*o*-cresol; bisphenols such as 2,2'-methylene bis(4-methyl-6-*t*-butylphenol), 2,2'-methylene bis(4-ethyl-6-*t*-butylphenol), 4,4'-thiobis(3-methyl-6-*t*-butylphenol), 4,4'-butylidene bis(3-methyl-6-*t*-butylphenol), triethylene glycol-bis[3-(3-*t*-butyl-5-methyl-4-hydroxyphenyl)propionate], 1,6-hexanediol-bis[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate], *N,N'*-hexamethylene bis(3,5-di-*t*-butyl-4-hydroxy-hydrocinnamamide), 2,2-thio-diethylene bis[3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate], 3,5-di-*t*-butyl-4-hydroxybenzylphosphonate-diethyl ester, 3,9-bis[1,1-dimethyl-2-{beta-(3-*t*-butyl-4-hydroxy-5-methylphenyl)propionyloxy}ethyl]2,4,8,10-tetraoxaspiro[5,5]undecane and bis(3,5-di-*t*-butyl-4-hydroxybenzyl sulfonic acid ethyl)calcium; and high-molecular phenols such as 1,1,3-tris(2-methyl-4-hydroxy-5-*t*-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene, tetrakis-[methylene-3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)propionate]methane, bis[3,3'-bis-(4'-hydroxy-3'-*t*-butylphenyl)butyric acid]glycol ester, tris-(3,5-di-*t*-butyl-4-hydroxy benzyl)-isocyanurate, 1,3,5-tris(3',5'-di-*t*-butyl-4'-hydroxy benzyl)-*S*-triazine-2,4,6-(1*H*, 3*H*, 5*H*)trione and tocopherol.

[0079]

Specific examples of the sulfur-type antioxidant are exemplified by dilauryl-3,3'-thiodipropionate, dimyristyl-3,3'-thiodipropionate, distearyl-3,3'-thiodipropionate and the like.

[0080]

Specific examples of the phosphorus antioxidant are exemplified by phosphites such as triphenyl phosphite, diphenyl isodecyl phosphite, phenyl diisodecyl phosphite, tris(nonylphenyl)phosphite, diisodecyl pentaerythritol phosphite, tris(2,4-di-t-butylphenyl)phosphite, cyclic neopentanetetrayl bis(octadecyl)phosphite, cyclic neopentanetetrayl bis(2,4-di-t-butylphenyl)phosphite, cyclic neopentanetetrayl bis(2,4-di-t-butyl-4-methylphenyl)phosphite, bis[2-t-butyl-6-methyl-4-{2-(octadecyloxycarbonyl)ethyl}phenyl]hydrogen phosphite; oxaphosphaphenanthrene oxides such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, 10-(3,5-di-t-butyl-4-hydroxybenzyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, 10-decyloxy-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide; and the like.

[0081]

These antioxidants can be used alone but may be also used in combination of 2 or more kinds. Particularly in the present invention, phosphorus antioxidant is preferable. The use amount of the antioxidant is usually 0.008 to 1 part by weight and preferably 0.01 to 0.5 part by weight relative to 100 parts by weight of the resin component in the curable resin composition of the present invention.

[0082]

When the curable resin composition of the present invention is used for optical semiconductor sealants, a phosphor can be added according to necessity. The phosphor has an action of, for example, absorbing some blue light emitted from blue LED element and emitting yellow light of which wavelength is converted to form white light. The phosphor is dispersed in the curable resin composition in advance, and then an optical semiconductor is sealed therewith. The phosphor is not particularly limited and a conventionally known phosphor can be used, and it is exemplified by, for example, aluminate, thiogallate and orthosilicate and the like of rare earth elements. More specifically, it includes phosphors such as YAG phosphor,

TAG phosphor, orthosilicate phosphor, thiogallate phosphor and sulfide phosphor, and is exemplified by YAlO_3 : Ce, $\text{Y}_3\text{Al}_5\text{O}_{12}$: Ce, $\text{Y}_4\text{Al}_2\text{O}_9$: Ce, $\text{Y}_2\text{O}_2\text{S}$: Eu, $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$: Eu, $(\text{SrEu})\text{O} \cdot \text{Al}_2\text{O}_3$ and the like. As for the particle size of said phosphor, the particle size known in the art is used and the average particle size is 1 to 250 μm and particularly preferably 2 to 50 μm . When these phosphors are used, the addition amount is 1 to 80 parts by weight and preferably 5 to 60 parts by weight, relative to 100 parts by weight of the resin component.

[0083]

Preferable curable resin compositions of the present invention are as follows.

(I) A curable resin composition, wherein the reactive functional group-containing siloxane compound according to any one of the above (i) to (xix) (hereinafter referred to as siloxane compound (A) of the present invention or said siloxane compound (A)) and an epoxy compound other than said siloxane compound (A) (hereinafter also referred to as O-EPO), which may be optionally contained, are contained in a total amount of 30 to 90% by weight (hereinafter, % represents % by weight unless otherwise specifically noted) relative to the whole composition, and the rest is the curing agent (B).

(II) The curable resin composition according to the above (I), wherein the curing agent (B) is contained in the range of 0.2 to 1.5 equivalents relative to 1 equivalent of the epoxy group in said siloxane compound (A).

(III) The curable resin composition according to the above (I) or (II), wherein said siloxane compound (A) and O-EPO which may be optionally contained are contained in a total amount of 50 to 90% relative to the whole composition.

(IV) The curable resin composition according to any one of the above (I) to (III), wherein the ratio of said siloxane compound (A) relative to the total amount of said siloxane compound (A) and O-EPO which may be optionally contained is 50 to 100%.

(V) The curable resin composition according to any one of the above (I) to (IV), wherein the ratio of said siloxane compound (A) relative to the total amount of said siloxane compound (A) and O-EPO which may be optionally contained is 30 to 90%.

(VI) The curable resin composition according to any one of the above (I) to (V), wherein a curing accelerator is further contained in a ratio of 0.001 to 15 parts by weight relative to 10 parts by weight of said siloxane compound (A).

(VII) The curable resin composition according to any one of the above (I) to (VI), wherein the curing agent (B) is an acid anhydride compound or a carboxylic acid compound.

The above curable resin composition of the present invention can be obtained by uniformly mixing the above raw materials in any method

[0084]

The above curable resin composition of the present invention contains the siloxane compound (A) having a reactive functional group, the curing agent (B) and, according to necessity, the curing accelerator (C), and in said curable resin composition, another optional blending component may be further blended if necessary. Another optional blending component can include an inorganic filler, a colorant, a silicone resin, a leveling agent, a lubricant, a coupling agent, a light stabilizer, an antioxidant, phosphors and the like. These other blending components can be appropriately added in the range of 0 to 500 parts by weight relative to 100 parts by weight of the total amount of said siloxane compound (A) and the curing agent (B), and preferable is about 0 to 100 parts by weight. When a blend with another blending component is solid, it is mixed using a blending machine such as Henschel mixer, Nauta mixer and the like, and then kneaded using a kneader, an extruder or a heating roll at 80 to 120°C and cooled, followed by grinding to obtain in a powdered state. On the other hand, when the blend is liquid, it is uniformly dispersed using planetary mixer to give the curable resin composition of the present invention containing another blending component.

[0085]

In order to seal an optical semiconductor such as an LED, a photo sensor, a transceiver by using the thus-obtained composition of the present invention to obtain an optical semiconductor of the present invention, formation may be carried out by a

conventional molding method such as transfer molding, compression molding, injection molding and dispensing methods, and printing method.

In addition, the heating method to cure the resin composition for optical semiconductor sealing after formation is not particularly limited and a conventional known method such as hot-air circulation heating, infrared ray heating and high-frequency heating can be employed. As for curing conditions, heating is usually carried out at about 80 to 250°C in the range of 30 seconds to 15 hours, but there is no harm if the conditions are appropriately changed. Preferable conditions are that curing is carried out at 110 to 200°C, for example, a method of carrying out the first curing at 100 to 140°C and then carrying out the final curing at 130 to 200°C is preferable.

[0086]

Hereinafter, the present invention will be more specifically explained with reference to Synthesis Examples and Examples. In addition, the present invention is not limited to these Synthesis Examples and Examples. In this regard, each physical property value in Examples was measured by the following method.

(1) Molecular weight: the weight average molecular weight in terms of converting polystyrene was calculated by measuring under the below-described conditions by Gel Permeation Chromatography (GPC) method.

Conditions under GPC:

Manufacturer: Shimadzu Corporation;

Column: Guard column SHODEX GPC LF-G LF-804 (three columns);

Flow rate: 1.0 ml/min.;

Column temperature: 40°C;

Solvent used: THF (tetrahydrofuran);

Detector: RI (differential refractive detector).

(2) Epoxy equivalent: measured by the method described in JIS K-7236.

(3) Viscosity: measured at 25°C using E-type viscometer (TV-20) manufactured by Toki Sangyo Co., Ltd.

Examples

[0087]

Hereinafter, the present invention will be more specifically explained with reference to Synthesis Examples and Examples. In this regard, "part(s)" means "part(s) by weight" and "%" means "% by weight" respectively, in Synthesis Examples and Examples. In addition, as for the equivalents of alkoxy and silanol, when the unit is not described, it is "g/eq" in any case.

Example 1

(Example where reaction was carried out so that the ratio of the alkoxy group is 5.3 equivalents relative to 1 equivalent of the silanol group)

The first step reaction: Into a reaction container, 197.1 parts (alkoxy group equivalent: 82.1 g/eq) of beta-(3,4 epoxycyclohexyl)ethyltrimethoxysilane, 237.4 parts (silanol equivalent: 530 g/eq) of silanol-terminal dimethyl silicone oil having a weight average molecular weight of 1060 (value measured by GPC) and 21.3 parts (0.11 parts as KOH) of a solution of 0.5% potassium hydroxide (KOH) in methanol were placed, and the liquid temperature were raised to 75°C. After the temperature was raised, reaction was carried out under reflux at 75°C for 8 hours.

The silanol equivalent of 530 g/eq was calculated by dividing the weight average molecular weight of 1060 measured using GPC as the molecular weight of the silicone oil into halves because of having two silanol groups per molecule. Also in the following Examples, each silanol equivalent of the silanol-terminal silicone oil (b) was determined in the same manner.

The second step reaction: To the reaction liquid obtained above, 305 parts of methanol were added, 86.4 parts of a solution of 50% distilled water in methanol was added thereto dropwise over 60 minutes and then the mixture was reacted under reflux at 75°C for 8 hours. After completion of the reaction, the reaction liquid was neutralized with a 5% aqueous sodium dihydrogenphosphate solution and then the methanol was collected at 80°C by distillation. To the rest reaction liquid, 380 parts

of methylisobutylketone (MIBK) were added and then water washing was repeated 3 times. Subsequently, the organic phase was separated and then the solvent was removed therefrom under reduced pressure at 100°C to obtain 344 parts of a block-type siloxane compound having a reactive functional group (A-1). As for the obtained compound, the epoxy equivalent was 457 g/eq, the weight average molecular weight was 3700, the viscosity was 600 mPa·s, and the appearance was colorless and transparent.

In addition, the ratio of the silicon atom belonging to the silsesquioxane segment (ratio of the silicon atom bonding to the 3 oxygen atoms relative to the total silicon atoms, which was calculated from the ratio of the added raw materials) was 19.6% by mol. Likewise, the ratio of the silicon atom belonging to the chain silicone segment was 80.4% by mol.

[0088]

Example 2

(Example where reaction was carried out so that the ratio of the alkoxy group was 30.8 equivalents relative to 1 equivalent of the silanol group)

The first step reaction: Into a reaction container, 197.1 parts (alkoxy group equivalent: 82.1) of beta-(3,4 epoxycyclohexyl)ethyltrimethoxysilane, 237.4 parts (silanol equivalent: 3060) of silanol-terminal dimethyl silicone oil having a weight average molecular weight of 6120 (value measured by GPC) and 20.0 parts (as KOH, 0.1 part) of a solution of 0.5% KOH in methanol were placed, and the liquid temperature was raised to 75°C. After the temperature was raised, reaction was carried out under reflux at 75°C for 8 hours.

As the second step reaction, after adding 260 parts of methanol, 86.4 parts of a solution of 50% distilled water in methanol were added dropwise over 60 minutes and the mixture was reacted under reflux at 75°C for 8 hours. After completion of the reaction, the reaction liquid was neutralized with a 5% aqueous sodium dihydrogenphosphate solution and then the methanol was collected by distillation at 80°C. Thereto, 380 parts of MIBK were added and water washing was repeated 3

times. Subsequently, the solvent was removed from the organic phase under reduced pressure at 100°C to obtain 360 parts of a block-type siloxane compound (A-2) having a reactive functional group. As for the obtained compound, the epoxy equivalent was 468 g/eq, the weight average molecular weight was 4160, the viscosity was 481 mPa·s, and the appearance was colorless and transparent.

In addition, the ratio of the silicon atom belonging to the silsesquioxane segment was 19.6% by mol. Likewise, the ratio of the silicon atom belonging to the chain silicone segment was 80.4% by mol.

[0089]

Example 3

(Example where reaction was carried out so that the ratio of the alkoxy group was 80.1 equivalents relative to 1 equivalent of the silanol group)

The first step reaction: Into a reaction container, 98.6 parts (alkoxy group equivalent: 82.1) of beta-(3,4 epoxycyclohexyl)ethyltrimethoxysilane, 118.7 parts (silanol equivalent: 7900) of silanol-terminal dimethyl silicone oil having a weight average molecular weight of 15800 (value measured by GPC) and 10.0 parts (as KOH, 0.05 part) of a solution of 0.5% KOH in methanol were placed, and the liquid temperature was raised to 75°C. After the temperature was raised, reaction was carried out under reflux at 75°C for 8 hours.

The second step reaction: After adding 142 parts of methanol, 43.2 parts of a solution of 50% distilled water in methanol were added dropwise over 60 minutes and the mixture was reacted under reflux at 75°C for 8 hours. After completion of the reaction, the reaction liquid was neutralized with a 5% aqueous sodium dihydrogenphosphate solution and then the methanol was collected by distillation at 80°C. Thereto, 191 parts of MIBK were added and water washing was repeated 3 times. Subsequently, the solvent was removed from the organic phase under reduced pressure at 100°C to obtain 169 parts of a block-type siloxane compound (A-3) having a reactive functional group. As for the obtained compound, the epoxy equivalent was 447 g/eq, the weight average molecular weight was 4130, the

viscosity was 710 mPa·s, and the appearance was colorless and transparent.

In addition, the ratio of the silicon atom belonging to the silsesquioxane segment was 19.6% by mol. Likewise, the ratio of the silicon atom belonging to the chain silicone segment was 80.4% by mol.

[0090]

Example 4

(Example where reaction was carried out so that the ratio of the alkoxy group was 8.6 equivalents relative to 1 equivalent of the silanol group)

The first step reaction: Into a reaction container 49.3 parts (alkoxy group equivalent: 82.1) of beta-(3,4 epoxycyclohexyl)ethyltrimethoxysilane, 39.7 parts (alkoxy group equivalent: 66.1) of phenyltrimethoxysilane, 118.7 parts (silanol equivalent: 850) of silanol-terminal methyl phenyl silicone oil having a weight average molecular weight of 1700 (value measured by GPC) and 10.0 parts (as KOH, 0.05 part) of a solution of 0.5% KOH in methanol were placed, and the liquid temperature was raised to 75°C. After the temperature was raised, reaction was carried out under reflux at 75°C for 8 hours.

The second step reaction: After adding 123 parts of methanol, 43.2 parts of a solution of 50% distilled water in methanol were added dropwise over 60 minutes and the mixture was reacted under reflux at 75°C for 8 hours. After completion of the reaction, the reaction liquid was neutralized with a 5% aqueous sodium dihydrogenphosphate solution and then the methanol was collected by distillation at 80°C. Thereto, 191 parts of MIBK were added and water washing was repeated 3 times. Subsequently, the solvent was removed from the organic phase under reduced pressure at 100°C to obtain 168 parts of a block-type siloxane compound (A-4) having a reactive functional group. As for the obtained compound, the epoxy equivalent was 874 g/eq, the weight average molecular weight was 2630, the viscosity was 4600 mPa·s, and the appearance was colorless and transparent.

In addition, the ratio of the silicon atom belonging to the silsesquioxane segment was 22.5% by mol. Likewise, the ratio of the silicon atom belonging to the

chain silicone segment was 77.5% by mol.

[0091]

Example 5

(Example where reaction was carried out so that the ratio of the alkoxy group was 8.6 equivalents relative to 1 equivalent of the silanol group)

The first step reaction: Into a reaction container 49.3 parts (alkoxy group equivalent: 82.1) of beta-(3,4 epoxycyclohexyl)ethyltrimethoxysilane, 27.2 parts (alkoxy group equivalent: 45.4) of methyltrimethoxysilane, 118.7 parts (silanol equivalent: 850) of silanol-terminal methyl phenyl silicone oil having a weight average molecular weight of 1700 (value measured by GPC) and 10.0 parts (as KOH, 0.05 part) of a solution of 0.5% KOH in methanol were placed, and the liquid temperature was raised to 75°C. After the temperature was raised, reaction was carried out under reflux at 75°C for 8 hours.

The second step reaction: After adding 123 parts of methanol, 43.2 parts of a solution of 50% distilled water in methanol were added dropwise over 60 minutes and the mixture was reacted under reflux at 75°C for 8 hours. After completion of the reaction, the reaction liquid was neutralized with a 5% aqueous sodium dihydrogenphosphate solution and then the methanol was collected by distillation at 80°C. Thereto, 166 parts of MIBK were added and water washing was repeated 3 times. Subsequently, the solvent was removed from the organic phase under reduced pressure at 100°C to obtain 151 parts of a block-type siloxane compound (A-5) having a reactive functional group. As for the obtained compound, the epoxy equivalent was 832 g/eq, the weight average molecular weight was 5850, the viscosity was 4610 mPa·s, and the appearance was colorless and transparent.

In addition, the ratio of the silicon atom belonging to the silsesquioxane segment was 20.0% by mol. Likewise, the ratio of the silicon atom belonging to the chain silicone segment was 80.0% by mol.

[0092]

Comparative Example 1

(Example where reaction was carried out so that the ratio of the alkoxy group was 1.4 equivalents relative to 1 equivalent of the silanol group: Example of gelation in the first step reaction)

Into a reaction container, 37.0 parts (alkoxy group equivalent: 82.1) of beta-(3,4 epoxycyclohexyl)ethyltrimethoxysilane, 170.9 parts (silanol equivalent: 530) of silanol-terminal dimethyl silicone oil having a weight average molecular weight of 1060 (value measured by GPC) and 12.3 parts (as KOH, 0.06 part) of a solution of 0.5% KOH in methanol were placed, and the liquid temperature was raised to 75°C. After the temperature was raised, when the reaction liquid was reacted under reflux at 75°C for 4 hours, the reactant was a solvent-insoluble gelated product (A-6).

[0093]

Reference Example 1

(Example where reaction was carried out in the presence of water so that the ratio of the alkoxy group was 5.5 equivalents relative to 1 equivalent of the silanol group)

Into a reaction container, 98.6 parts (alkoxy group equivalent: 82.1) of beta-(3,4 epoxycyclohexyl)ethyltrimethoxysilane, 118.7 parts (silanol equivalent: 530) of silanol-terminal dimethyl silicone oil having a weight average molecular weight of 1060 (value measured by GPC), 131 parts of methanol and 10.0 parts (as KOH, 0.05 part) of a solution of 0.5% KOH in methanol were placed, and the liquid temperature was raised to 75°C. After the temperature was raised, 43.2 parts of a solution of 50% distilled water in methanol were added dropwise over 60 minutes and the mixture was reacted under reflux at 75°C for 8 hours. After completion of the reaction, the reaction liquid was neutralized with a 5% aqueous sodium dihydrogenphosphate solution and then the methanol was collected by distillation at 80°C. Thereto, 191 parts of MIBK were added and water washing was repeated 3 times. Subsequently, the solvent was removed from the organic phase under reduced pressure at 100°C to obtain 176 parts of a siloxane compound (A-7) having a reactive functional group. As for the obtained compound, the epoxy equivalent was 459 g/eq, the weight average molecular weight was 3300, and the appearance was

white-turbid, whereby it could not be used as a composition for optical semiconductor-sealing materials.

[0094]

Reference Example 2

(Example where reaction was carried out in the presence of water so that the ratio of the alkoxy group was 30.7 equivalents relative to 1 equivalent of the silanol group)

In the same manner as the synthesis method in Patent Literature 1, 45.4 parts (alkoxy group equivalent: 82.1) of beta-(3,4 epoxycyclohexyl)ethyltrimethoxysilane, 54.6 parts (silanol equivalent: 3060) of silanol-terminal dimethyl silicone oil having a weight average molecular weight of 6120 (value measured by GPC), 10.0 parts of triethylamine and 500 parts of MIBK were placed into a reaction container, 100 parts of distilled water were added dropwise at room temperature under stirring over 30 minutes, and after the temperature was raised to 80°C, the mixture was reacted for 6 hours. After completion of the reaction, the reaction liquid was neutralized with a 20% aqueous sodium dihydrogenphosphate solution and then water washing was repeated 3 times. Subsequently, the solvent was removed from the organic phase under reduced pressure at 100°C to obtain 85 parts of a white-turbid liquid (A-8), which could not be used as a composition for optical semiconductor-sealing materials.

[0095]

Reference Example 3

(Example where reaction was carried out in the presence of water so that the ratio of the alkoxy group was 31.0 equivalents relative to 1 equivalent of the silanol group)

Into a reaction container, 78.8 parts (alkoxy group equivalent: 82.1) of beta-(3,4 epoxycyclohexyl)ethyltrimethoxysilane, 94.0 parts (silanol equivalent: 3060) of silanol-terminal dimethyl silicone oil having a weight average molecular weight of 6120 (value measured by GPC), 104 parts of methanol and 8.0 parts (as KOH, 0.04 part) of a solution of 0.5% KOH in methanol were placed, and the liquid temperature was raised to 75°C. After the temperature was raised, 34.6 parts of a solution of

50% distilled water in methanol were added dropwise over 60 minutes and the mixture was reacted under reflux at 75°C for 8 hours. After completion of the reaction, the reaction liquid was neutralized with a 5% aqueous sodium dihydrogenphosphate solution and then the methanol was collected by distillation at 80°C. Thereto, 152 parts of MIBK were added and water washing was repeated 3 times. Subsequently, the solvent was removed from the organic phase under reduced pressure at 100°C to obtain 151 parts of a white-turbid liquid (A-9), which could not be used as a composition for optical semiconductor-sealing materials.

[0096]

Reference Example 4

(Example where reaction was carried out in the presence of water so that the ratio of the alkoxy group was 80.0 equivalents relative to 1 equivalent of the silanol group)

Into a reaction container, 98.6 parts (alkoxy group equivalent: 82.1) of beta-(3,4 epoxycyclohexyl)ethyltrimethoxysilane, 118.7 parts (silanol equivalent: 7900) of silanol-terminal dimethyl silicone oil having a weight average molecular weight of 15800 (value measured by GPC), 142 parts of methanol and 10.0 parts (as KOH, 0.05 part) of a solution of 0.5% KOH in methanol were placed, and the liquid temperature was raised to 75°C. After the temperature was raised, 43.2 parts of a solution of 50% distilled water in methanol were added dropwise over 60 minutes and the mixture was reacted under reflux at 75°C for 8 hours. After completion of the reaction, the reaction liquid was neutralized with a 5% aqueous sodium dihydrogenphosphate solution and then the methanol was collected by distillation at 80°C. Thereto, 191 parts of MIBK were added and water washing was repeated 3 times. Subsequently, the solvent was removed from the organic phase under reduced pressure at 100°C to obtain 189 parts of a white-turbid liquid (A-10).

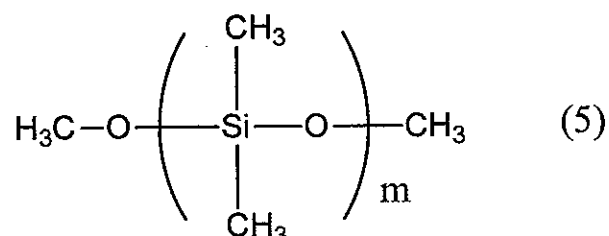
[0097]

Comparative Example 2

The synthesis was carried out using silicone oil having a terminal of an alkoxy group represented by the following formula (5), instead of silanol-terminal silicone oil

of the formula (2) used in Examples 1 to 5.

[0098]



[0099]

Into a reaction container, 37.0 parts (alkoxy group equivalent: 82.1) of beta-(3,4 epoxycyclohexyl)ethyltrimethoxysilane, 63.1 parts (alkoxy equivalent: 1250) of methoxy-terminal dimethyl silicone oil having a weight average molecular weight of 2500 (value measured by GPC), 64 parts of methanol and 5.0 parts (as KOH, 0.025 part) of a solution of 0.5% KOH in methanol were placed, and the liquid temperature was raised to 75°C. After the temperature was raised, 16.2 parts of a solution of 50% distilled water in methanol were added dropwise over 60 minutes and the mixture was reacted under reflux at 75°C for 8 hours. After completion of the reaction, the reaction liquid was neutralized with a 5% aqueous sodium dihydrogenphosphate solution and then the methanol was collected by distillation at 80°C. Thereto, 88 parts of MIBK were added and water washing was repeated 3 times. Subsequently, the solvent was removed from the organic phase under reduced pressure at 100°C to obtain 80.6 parts of a white-turbid liquid (A-11), which could not be used as a composition for optical semiconductor-sealing material.

[0100]

The properties of resins A-1 to A-11 obtained in Examples 1 to 5, Comparative Examples 1 to 2 and Reference Examples 1 to 4 are summarized in Table 1.

Table 1

Compound	Addition	Epoxy	Molecular	Property
	equivalent value	equivalent	weight	

(Alkoxy group /Silanol group)					
Example 1	A-1	5.3	457	3700	Colorless and transparent liquid
Example 2	A-2	30.8	468	4160	Colorless and transparent liquid
Example 3	A-3	80.1	447	4130	Colorless and transparent liquid
Example 4	A-4	8.6	874	2630	Colorless and transparent liquid
Example 5	A-5	8.6	832	5830	Colorless and transparent liquid
Comp. Exam. 1	A-6	1.4	-	-	Gelated product
Ref. Exam. 1	A-7	5.5	-	-	White-turbid liquid
Ref. Exam. 2	A-8	30.7	-	-	White-turbid liquid
Ref. Exam. 3	A-9	31.0	-	-	White-turbid liquid
Ref. Exam. 4	A-10	80.0	-	-	White-turbid liquid
Comp. Exam. 2	A-11	-	-	-	White-turbid liquid

Note: "Comp. Exam." represents "Comparative Example" and "Ref. Exam." represents "Reference Example".

[0101]

From the above results, it can be confirmed that Comparative Example 1 where the compound represented by the general formula (1) and the compound represented by the general formula (2) were added in an alkoxy group/silanol group equivalent value of 1.4 was a solvent-insoluble gelated product and cannot be used as an epoxy resin. In addition, it can be confirmed that Reference Example 1, Reference Example 2, Reference Example 3 and Reference Example 4 (A-7, A-8, A-9 and A-10) where the compound represented by the general formula (1) and the compound

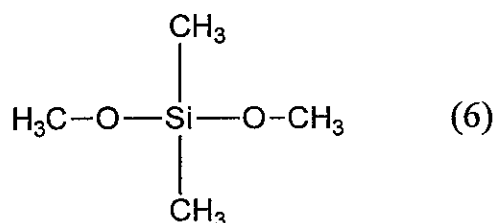
represented by the general formula (2) were added at a time together with an alkali catalyst and water for synthesis were white-turbid liquids and not suitable for optics application. Further, it can be found that A-11 (Comparative Example 2) where the compound of the formula (5) as silicone oil having a terminal of an alkoxy group was used as a chain silicone segment instead of the compound represented by the general formula (2) was also a white-turbid liquid and not suitable for optics application. On the other hand, it can be confirmed that Examples 1 to 3 (A-1, A-2 and A-3) where the compounds represented by the general formula (1) and the general formula (2) were reacted in 2 steps and Examples 4 to 5 (A-4 and A-5) where the compounds represented by the general formulas (1), (2) and (3) were reacted in 2 steps gave colorless and transparent resins and were suitable for optics application.

[0102]

Comparative Example 3

The synthesis was carried out using dimethyldimethoxysilane of the following formula (6) as a raw material so that the content concentration (% by mol) of dimethylsiloxane unit structure contained in the compound was the same concentration (% by mol) as in the above Examples 1 to 3 when regarding dimethylsiloxane as a unit structure.

[0103]



[0104]

In the same manner of synthesis as described in Patent Literature 1, 33.9 parts (alkoxy group equivalent: 82.1) of beta-(3,4 epoxycyclohexyl)ethyltrimethoxysilane, dimethyldimethoxysilane (alkoxy equivalent: 60.1), 10.0 parts of triethylamine and 500 parts of MIBK were added to a reaction container, 100 parts of distilled water were added dropwise at room temperature under stirring over 30 minutes, and after

the temperature was raised to 80°C, the mixture was reacted for 6 hours. After completion of the reaction, the reaction liquid was neutralized with a 20% aqueous sodium dihydrogenphosphate solution and then water washing was repeated 3 times. Subsequently, the solvent was removed from the organic phase under reduced pressure at 100°C to obtain 60 parts of a siloxane compound (A-12) having a reactive functional group. As for the obtained compound, the epoxy equivalent was 459 g/eq, the weight average molecular weight was 940, and the appearance was colorless and transparent.

[0105]

Example 6

(Example where reaction was carried out so that the ratio of the alkoxy group was 3.8 equivalents relative to 1 equivalent of the silanol group)

The first step reaction: To a reaction container, 147.8 parts (alkoxy group equivalent: 82.1) of beta-(3,4 epoxycyclohexyl)ethyltrimethoxysilane, 252.8 parts (silanol equivalent: 356) of silanol-terminal dimethyl silicone oil having a weight average molecular weight of 1060 (value measured by GPC) and 20.0 parts (as KOH, 0.1 part) of a solution of 0.5% KOH in methanol were added, and the liquid temperature was raised to 75°C. After the temperature was raised, reaction was carried out under reflux at 75°C for 8 hours.

The second step reaction: After adding 255 parts of methanol, 64.8 parts of a solution of 50% distilled water in methanol were added dropwise over 60 minutes and the mixture was reacted under reflux at 75°C for 8 hours. After completion of the reaction, the reaction liquid was neutralized with a 5% aqueous sodium dihydrogenphosphate solution and then the methanol was collected by distillation at 80°C. Thereto, 352 parts of MIBK were added and water washing was repeated 3 times. Subsequently, the solvent was removed from the organic phase under reduced pressure at 100°C to obtain 333 parts of a block-type siloxane compound (A-13) having a reactive functional group. As for the obtained compound, the epoxy equivalent was 578 g/eq, the weight average molecular weight was 5250, the

viscosity was 257 mPa·s, and the appearance was colorless and transparent.

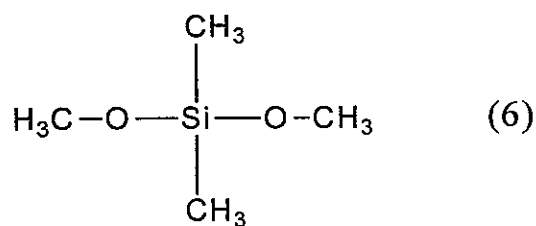
In addition, the ratio of the silicon atom belonging to the silsesquioxane segment was 14.9% by mol. Likewise, the ratio of the silicon atom belonging to the chain silicone segment was 85.1% by mol.

[0106]

Comparative Example 4

The synthesis was carried out using dimethyldimethoxysilane of the following formula (6) as a raw material so that the content concentration (% by mol) of dimethylsiloxane unit structure contained in the compound was same concentration (% by mol) as in the above Example 6 when regarding dimethylsiloxane as a unit structure.

[0107]



[0108]

In the same manner of synthesis as described in Patent Literature 1, 26.6 parts (alkoxy group equivalent: 82.1) of beta-(3,4 epoxycyclohexyl)ethyltrimethoxysilane, 73.4 parts (alkoxy equivalent: 60.1) of dimethyldimethoxysilane, 10.0 parts of triethylamine and 500 parts of MIBK were added to a reaction container, 100 parts of distilled water were added dropwise at room temperature under stirring over 30 minutes, and after the temperature was raised to 80°C, the mixture was reacted for 6 hours. After completion of the reaction, the reaction mixture was neutralized with a 20% aqueous sodium dihydrogenphosphate solution and then water washing was repeated 3 times. Subsequently, the solvent was removed from the organic phase under reduced pressure at 100°C to obtain 60 parts of a siloxane compound (A-14) having a reactive functional group. As for the obtained compound, the epoxy equivalent was 561 g/eq, the weight average molecular weight was 830, and the

appearance was colorless and transparent.

[0109]

Example 7

(Example where reaction was carried out so that the ratio of the alkoxy group was 4.8 equivalents relative to 1 equivalent of the silanol group)

The first step reaction: To a reaction container, 59.1 parts (alkoxy group equivalent: 82.1) of beta-(3,4 epoxycyclohexyl)ethyltrimethoxysilane, 130.6 parts (silanol equivalent: 850) of silanol-terminal methyl phenyl silicone oil having a weight average molecular weight of 1700 (value measured by GPC) and 10.0 parts (as KOH, 0.1 part) of a solution of 0.5% KOH in methanol were added, and the liquid temperature was raised to 75°C. After the temperature was raised, reaction was carried out under reflux at 75°C for 8 hours.

The second step reaction: After adding 135 parts of methanol, 25.9 parts of a solution of 50% distilled water in methanol were added dropwise over 60 minutes and the mixture was reacted under reflux at 75°C for 8 hours. After completion of the reaction, the reaction liquid was neutralized with a 5% aqueous sodium dihydrogenphosphate solution and the methanol was collected by distillation at 80°C. After that, 170 parts of MIBK were added to wash and water washing was repeated 3 times. Subsequently, the solvent was removed from the organic phase under reduced pressure at 100°C to obtain 162 parts of a block-type siloxane compound (A-15) having a reactive functional group. As for the obtained compound, the epoxy equivalent was 707 g/eq, the weight average molecular weight was 2680, the viscosity 727 mPa·s, and the appearance was colorless and transparent.

In addition, the ratio of the silicon atom belonging to the silsesquioxane segment was 13.6% by mol. Likewise, the ratio of the silicon atom belonging to the chain silicone segment was 86.4% by mol.

[0110]

Examples 8 to 13 and Comparative Examples 5 to 7

The above-synthesized siloxane compound (any one of A-1 to 3 and 12 to 15)

or a commercially available alicyclic-type epoxy resin (ERL-4221) conventionally used for optical semiconductor sealing was mixed with a curing agent (B-1 to B-3) or with both a curing agent (B-3) and a curing accelerator C-1, in an amount of the parts by weight shown in Table 2, 3, 4 or 5 to obtain compositions of Examples 8 to 13 of the present invention and Comparative Examples 5 to 7.

Examples and Comparative Examples described in Table 2 are as below:

Example 8: A composition using the compound A-1 and the curing agent B-1;

Example 9: A composition using the compound A-2 and the curing agent B-1;

Example 10: A composition using the compound A-3 and the curing agent B-1;

Comparative Example 5: A composition using the compound A-12 and the curing agent B-1;

Comparative Example 6: A composition using ERL-4221 and the curing agent B-1.

Example and Comparative Example described in Table 3 are as below:

Example 11: A composition using the compound A-13, the curing agent B-3 and the curing accelerator C-1;

Comparative Example 7: A composition using the compound A-14, the curing agent B-3 and the curing accelerator C-1.

Example and Comparative Example described in Table 4 are as below:

Example 12: A composition using the compound A-15, the curing agent B-3 and the curing accelerator C-1.

Example and Comparative Example described in Table 5 are as below:

Example 13: A composition using the compound A-13, the curing agent B-3 and the curing accelerator C-1;

Comparative Example 6: A composition using ERL-4221 and the curing agent B-1.

[0111]

Transmittance test, mechanical property test (dynamic viscoelasticity test) and LED lighting test below-described were carried out on the curable resin compositions obtained in Examples 8 to 13 and Comparative Examples 5 to 7, and the results thereof are shown in Tables 2, 3, 4 and 5.

[0112]

(UV resistance transmittance test)

Each curable resin composition obtained in Examples 8 to 13 and Comparative Examples 5 to 7 was subjected to vacuum defoaming for 20 minutes and then gently cast-molded into an aluminum cup having a base diameter of 5 cm and a height of 2 cm. The cast-molded product was placed into an oven and cured under predetermined curing conditions to obtain a test piece having a thickness of 2 mm for transmittance test. Using these test pieces, transmittance ratio before and after ultraviolet irradiation (measurement wavelength: 375 nm, 400 nm and 465 nm) was measured by a spectrophotometer and the changing ratio was calculated.

The ultraviolet irradiation conditions are as follows:

Ultraviolet irradiation machine: Eye Super UV tester SUV-W11;

Temperature: 60°C;

Irradiation energy: 65 mW/cm²;

Irradiation hours: 100 hours.

[0113]

(Heat durability transmittance test)

Each curable resin compositions obtained in Examples 8 to 13 and Comparative Examples 5 to 7 was subjected to vacuum defoaming for 20 minutes and then gently cast-molded into an aluminum cup having a base diameter of 5 cm and a height of 2 cm. The cast-molded product was placed into an oven and cured under predetermined curing conditions to obtain a test piece having a thickness of 2 mm for transmittance test. Using these test pieces, transmittance ratio before and after being left in an oven at 150°C for 96 hrs (measurement wavelength: 375 nm, 400 nm and 465 nm) was measured by a spectrophotometer and the changing ratio was calculated.

[0114]

(Mechanical property test)

Each curable resin composition obtained in Examples 8 to 13 and Comparative

Examples 5 to 7 was subjected to vacuum defoaming for 20 minutes and then gently cast-molded into a mold for test pieces having a width of 7 mm, a length of 5 cm and a thickness of about 800 μm , and after that, a lid of polyimide film was put onto the mold. The cast-molded product was cured under the conditions described in Tables 2 and 3 to obtain a test piece for dynamic viscoelasticity. Using these test pieces, dynamic viscoelasticity test was carried out under the below conditions.

Measurement conditions:

Dynamic viscoelasticity measuring instrument: DMA-2980 manufactured by TA-instruments;

Measurement temperature range: -30°C to 280°C ;

Rate of temperature rise: $2^{\circ}\text{C}/\text{minute}$;

Test piece size: A piece cut into a size of 5 mm $\times$ 50 mm (thickness of about 800 μm) was used.

Analysis conditions:

T_g: The peak point of Tan-delta in DMA measurement was T_g;

Elastic modulus at -30°C : Elastic modulus at -30°C was measured.

[0115]

(LED lighting test)

Each curable resin composition obtained in Examples 8 to 13 and Comparative Examples 5 to 7 was subjected to vacuum defoaming for 20 minutes and then filled in a syringe, and using a precisely discharging apparatus, it was cast-molded into a surface mounting-type LED mounting a light-emitting element having a emission wavelength of 375 nm. After that, it was cured under predetermined curing conditions to obtain an LED for lighting test. The lighting test is carried out under accelerated conditions, so lighting test was carried out at 60 mA which is three times the specified current. The specific conditions are shown below. As for measurement items, illuminance before and after 100 hour lighting was measured using an integrating sphere, and the retention ratio of illuminance was calculated. In addition, the state of the light-emitting element surface after 100 hour lighting was

observed.

Specific lighting conditions:

Emission wavelength: 375 nm;

Driving system: Constant-current system, 60 mA (light-emitting element specified current; 20 mA);

Driving environment: 25°C, 65%.

[0116]

Table 2

	Example 8	Example 9	Example 10	Comp. Exam. 5	Comp. Exam. 6
(Blend)					
Compound A-1	100	-	-	-	-
Compound A-2	-	100			
Compound A-3	-	-	100	-	-
Compound A-12	-	-	-	100	-
ERL-4221	-	-	-	-	100
Curing agent B-1	30.5	30.0	31.1	30.3	-
Curing agent B-2	-	-	-	-	71.8
(Mechanical property test)					
Tg	113	113	116	92	254
Elastic modulus	1449	1515	1615	1801	4567
at -30°C					
Surface tackiness	None	None	None	None	None
(UV resistance transmittance test)					
375 nm	95%	95%	95%	94%	72%
Transmittance retention ratio					
400 nm	98%	98%	98%	96%	76%
Transmittance retention ratio					
465 nm	100%	100%	100%	99%	90%
Transmittance retention ratio					

Note: "Comp. Exam." represents "Comparative Example".

[0117]

* Curing agent B-1: As a curing agent, a mixture of 30 parts of 1,3,4-cyclohexanetricarboxylic acid-3,4-anhydride ("H-TMA", manufactured by Mitsubishi Gas Chemical Company, INC.) and 70 parts of "MH-700G" (manufactured by New Japan Chemical Co., Ltd.) as a mixture of methylhexahydrophthalic acid anhydride and hexahydrophthalic acid anhydride was prepared in advance, and it was used as a curing agent B-1.

* Curing agent B-2: As a curing agent, a mixture of 50 parts of 1,3,4-cyclohexanetricarboxylic acid-3,4-anhydride ("H-TMA", manufactured by Mitsubishi Gas Chemical Company, INC.) and 50 parts of "MH-700G" (manufactured by New Japan Chemical Co., Ltd.) as a mixture of methylhexahydrophthalic acid anhydride and hexahydrophthalic acid anhydride was prepared in advance, and it was used as a curing agent B-2.

* ERL-4221: Alicyclic-type epoxy resin manufactured by The Dow Chemical Company.

* Curing condition: 120°C for 2 hrs + 140°C for 2 hrs (Examples 8, 9 and 10 and Comparative Examples 5 and 6).

* The unit of Tg is [°C] and the unit of elastic modulus at -30°C is [MPa].

[0118]

From the above results, it is found that the curable resin compositions of Examples 8 to 10 using the siloxane compound (A) of the present invention synthesized in the 2-step reaction have a higher Tg and an excellent heat resistance and also have reduced elastic modulus at low temperature compared with Comparative Example 5 using a compound likewise having the same content concentration (% by mol) of dimethylsiloxane unit structure, and are excellent in heat resistance and low elastic modulus properties. In addition, it can be confirmed to be more excellent in light fastness and low elastic modulus properties than Comparative Example 6 as a conventional alicyclic epoxy resin.

[0119]

Table 3

	Example 11	Comparative Example 7
(Blend)		
Compound A-13	100	-
Compound A-14	-	100
Curing agent B-3	28.9	29.9
Curing accelerator C-1	0.1	0.1
(Mechanical property test)		
T _g	57°C	*2)
Elastic modulus at -30°C	1139	*2)
Surface tackiness	None	*2)
(UV resistance transmittance test)		
375 nm	94.6%	93.8%
Transmittance retention ratio		
400 nm	99.0%	97.2%
Transmittance retention ratio		
465 nm	100%	100%
Transmittance retention ratio		
(Heat durability transmittance test)		
375 nm	97.4%	84.0%
Transmittance retention ratio		
400 nm	99.1%	89.4%
Transmittance retention ratio		
465 nm	100%	96.1%
Transmittance retention ratio		
(Weight change after cured)*3)		
Weight retention ratio	95%	91%

* Curing agent B-3: A mixture of methylhexahydrophthalic acid anhydride and

hexahydrophthalic acid anhydride was used ("MH-700G", manufactured by New Japan Chemical Co., Ltd.).

* Curing accelerator C-1: "U-CAT 18X" (which is a trade name) commercially available from San-Apro Ltd. was used as a reaction accelerator for epoxy resin and acid anhydride.

* Curing condition: 120°C for 2 hrs + 140°C for 2 hrs, for all.

* The unit of Tg is [°C] and the unit of elastic modulus at -30°C is [MPa].

* 2) There was a trace of foaming, and an appropriate sample as a cured product for dynamic viscoelasticity could not be obtained.

*3) A trace of foaming of Comparative Example 7 was confirmed in *2), and therefore the reduction amount of resin was measured in making a sample for UV resistance transmittance property test and the weight retention ratio was confirmed.

In this regard, the weight retention ratio was calculated by (weight of cast-molded product after curing / weight of cast-molded product before curing) × 100.

[0120]

As for the curable resin composition of Comparative Example 7, a trace of foaming was generated and a cured product for dynamic viscoelasticity measurement could not be normally made, while as for the curable resin composition of Example 11, a cured product without tackiness properties could be made and it is found to be a cured product having a low elastic modulus. In addition, the reduction amount of resin in each sample for UV resistance transmittance property test was measured before and after curing, resulting that the curable resin composition of Comparative Example 7 had 9% reduced amount while the curable resin composition of Example 11 had only about 5% reduced amount, the curable resin composition of the present invention has less reduction in the amount before and after curing, and the cast-molded product for LED packages have fewer dents after curing, whereby it is found that the curable resin composition of the present invention is also suitable as a composition for LED sealing in this respect. Further, Example 11 is also excellent in

UV resistance and heat resistance of transmittance ratio, compared with Comparative Example 7.

[0121]

Table 4

	Example 12
(Blend)	
Compound A-15	100
Curing agent B-3	21.4
Curing accelerator C-1	0.1
(Mechanical property test)	
Tg	45°C
Elastic modulus at -30°C	1539
Surface tackiness	None
(UV resistance transmittance test)	
375 nm	88.1%
Transmittance retention ratio	
400 nm	93.9%
Transmittance retention ratio	
465 nm	99.2%
Transmittance retention ratio	

[0122]

* Curing agent B-3: A mixture of methylhexahydrophthalic acid anhydride and hexahydrophthalic acid anhydride was used ("MH-700G", manufactured by New Japan Chemical Co., Ltd.).

* Curing accelerator C-1: "U-CAT 18X" (which is a trade name) commercially available from San-Apro Ltd. was used as a reaction accelerator for epoxy resin and acid anhydride.

* Curing conditions: 120°C for 1 hr + 150°C for 3 hrs.

* The unit of Tg is [°C] and the unit of elastic modulus at -30°C is [MPa].

It is found that the curable resin composition of Example 12 using the siloxane compound (A) of the present invention synthesized in the 2-step reaction becomes a cured product having a low elastic modulus even at low temperature.

[0123]

Table 5

	Example 13	Comparative Example 6	Non-sealed
(Blend)			
Compound A-13	100	-	-
ERL-4221	-	100	-
Curing agent B-2	-	71.8	-
Curing agent B-3	29.1	-	-
Curing accelerator C-1	0.1	-	-
(UV resistance transmittance test)			
375 nm	92.5%	72%	-
Transmittance retention ratio			
400 nm	96.5%	76%	-
Transmittance retention ratio			
465 nm	99.7%	90%	-
Transmittance retention ratio			
(LED lighting test)			
Illuminance retention ratio	91%	21%	83%
State of element surface	Colorless	Brown	Colorless

[0124]

* In order to observe deterioration of the element itself, LED lighting test was carried out at the same time on a non-sealed LED where resin is not injected.

* Curing agent B-2: As a curing agent, a mixture of 50 parts of 1,3,4-cyclohexanetricarboxylic acid-3,4-anhydride ("H-TMA", manufactured by Mitsubishi Gas Chemical Company, INC.) and 50 parts of "MH-700G" (manufactured by New Japan Chemical Co., Ltd.) which is a mixture of methylhexahydrophthalic

acid anhydride and hexahydrophthalic acid anhydride was prepared in advance, and it was used as a curing agent B-2.

* Curing agent B-3: A mixture of methylhexahydrophthalic acid anhydride and hexahydrophthalic acid anhydride was used ("MH-700G", manufactured by New Japan Chemical Co., Ltd.).

* Curing accelerator C-1: "U-CAT 18X" (which is a trade name) commercially available from San-Apro Ltd. was used as a reaction accelerator for epoxy resin and acid anhydride.

*ERL-4221: Alicyclic-type epoxy resin manufactured by The Dow Chemical Company.

* Curing condition: 110°C for 6 hrs (Example 13).

* Curing condition: 120°C for 1 hr + 150°C for 3 hrs (Comparative Example 6).

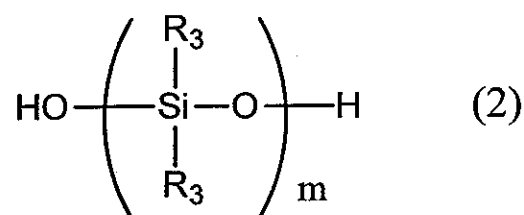
* The unit of T_g is [°C] and the unit of elastic modulus at -30°C is [MPa].

[0125]

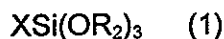
From the above results, it is found that when the curable resin composition of Example 13 using the siloxane compound (A) of the present invention synthesized in the 2-step reaction is used for LED-sealing materials, its illuminance retention ratio is apparently more excellent than that of the curable resin composition of Comparative Example 6 using a conventional alicyclic epoxy resin. From this, it can be confirmed that the curable resin composition of the present invention is suitable as an LED-sealing material.

CLAIMS

1. A reactive functional group-containing block-type-siloxane compound having a chain silicone segment and a hydrolysis condensation segment of tri(C1-C10)alkoxysilane having a group selected from the group consisting of a reactive functional group having an epoxy group, a methyl group and a phenyl group, at least one of the hydrolysis condensation segments being a segment containing at least one reactive functional group having an epoxy group, which is obtained by, as a first step reaction, reacting silanol-terminal silicone oil (b) represented by the general formula (2):



(wherein, plural existing R₃ may be the same or different from each other and each represents a straight chain, branched or cyclic alkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 14 carbon atoms or an alkenyl group having 2 to 10 carbon atoms, and m represents 2 to 2000 as an average value) with an alkoxysilane compound (a) represented by the general formula (1):



(wherein, X represents a reactive functional group having an epoxy group, and R₂ represents an alkyl group having 1 to 10 carbon atoms)

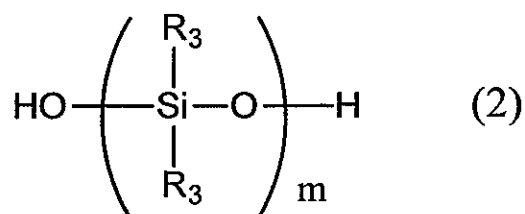
in the range that the alkoxy group equivalent of the alkoxysilane compound is 1.5 to 200

equivalents relative to 1 equivalent of the silanol group of the silanol-terminal silicone oil (b) for condensation to form an alkoxysilane modified form (d), and then by, as a second step reaction, adding water to the resulting reaction liquid for hydrolysis- condensation of alkoxy groups in both the above alkoxysilane modified form (d) and the alkoxysilane compound(a) in the coexistence of the alkoxysilane compound (a).

2. The reactive functional group-containing block-type-siloxane compound according to Claim 1, wherein the hydrolysis condensation segment is a silsesquioxane segment.

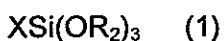
3. The reactive functional group-containing block-type-siloxane compound according to Claim 2, wherein m is 2 to 200.

4. A reactive functional group-containing block-type-siloxane compound which is a block-type siloxane oligomer having a chain silicone segment and a hydrolysis condensation segment of tri(C1-C10)alkoxysilane having a group selected from the group consisting of a reactive functional group having an epoxy group, a methyl group and a phenyl group, at least one of the hydrolysis condensation segments being a segment containing at least one reactive functional group having an epoxy group, which is obtained by, as the first step reaction, reacting silanol-terminal silicone oil (b) represented by the general formula (2):



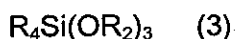
(wherein, plural existing R_3 may be the same or different from each other and each represents a straight chain, branched or cyclic alkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 14 carbon atoms or an alkenyl group having 2 to 10 carbon atoms, and m represents 2 to 200 as an average value)

with both an alkoxysilane compound (a) represented by the general formula (1):



(wherein, X represents a reactive functional group having an epoxy group and each R_2 represents an alkyl group having 1 to 10 carbon atoms)

and an alkoxysilane compound (c) represented by the general formula (3):



(wherein, R_4 represents a methyl group or a phenyl group, and R_2 may be the same or different from R_2 in the general formula (1) and each independently represents an alkyl group having 1 to 10 carbon atoms)

in the range that the total equivalent of the alkoxy group in the alkoxysilane compounds (a) and (c) is 1.5 to 200 equivalents relative to 1 equivalent of the silanol group in the silanol-terminal silicone oil (b) for condensation to form an alkoxysilane modified form (d), and then by, as the second step reaction, adding water to the obtained reaction liquid for hydrolysis- condensation of alkoxy groups in both the above alkoxysilane modified form (d) and the alkoxysilane (a) in the coexistence of alkoxysilane (a).

5. The reactive functional group-containing block-type-siloxane compound according to any one of Claims 1 to 4, wherein R_3 in the general formula (2) each independently

represents a methyl group or a phenyl group, R_2 in the general formula (1) each independently represents a methyl group or an ethyl group, and R_2 in the general formula (3) may be the same or different from R_2 in the general formula (1) and each independently represents a methyl group or an ethyl group.

6. The reactive functional group-containing block-type-siloxane compound according to any one of Claims 1 to 5, wherein X in the general formula (1) is an epoxycyclohexyl ethyl group.

7. The reactive functional group-containing block-type-siloxane compound according to any one of Claims 1 to 5, wherein the weight average molecular weight (Mw) of the silanol-terminal silicone oil (b) of the general formula (2) is 300 to 18,000.

8. The reactive functional group-containing block-type-siloxane compound according to any one of Claims 1 to, wherein the weight average molecular weight (Mw) is 800 to 20,000.

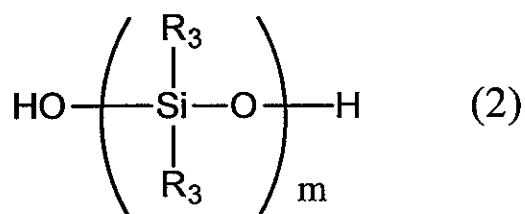
9. The reactive functional group-containing block-type-siloxane compound according to Claim 1 or 4, wherein the R_3 is a methyl group or a phenyl group.

10. The reactive functional group-containing block-type-siloxane compound according to Claim 2 or 10, which is characterized in that the reactive functional group having an epoxy group in the silsesquioxane segment contains an epoxycyclohexyl group.

11. The reactive functional group-containing block-type-siloxane compound according to any one of Claims 1 to 10, wherein the epoxy equivalence is 300 to 1600g/eq.

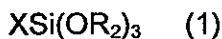
12. The reactive functional group-containing block-type-siloxane compound according to any one of Claims 1 to 10, wherein the silanol-terminal silicone oil (b) represented by the general formula (2) is a silanol-terminal methyl phenyl silicone oil.

13. A method for producing a reactive functional group-containing- block-type siloxane compound which is a block-type siloxane oligomer having a chain silicone segment and a hydrolysis condensation segment of tri(C1-C10)alkoxysilane having a group selected from the group consisting of a reactive functional group having an epoxy group, a methyl group and a phenyl group, at least one of the hydrolysis condensation segments being a segment containing at least one reactive functional group having an epoxy group, which is characterized by, as a first step reaction, reacting silanol-terminal silicone oil (b) represented by the general formula (2):



(wherein, plural existing R₃ may be the same or different from each other and each independently represents a straight chain, branched or cyclic alkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 14 carbon atoms or an alkenyl group having 2

to 10 carbon atoms, and m represents 2 to 2000 as an average value) with an alkoxysilane compound (a) represented by the general formula (1):



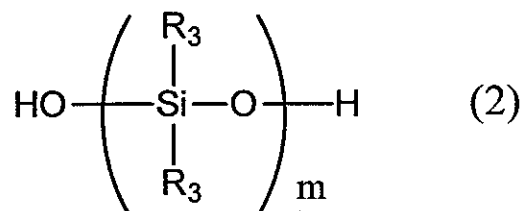
(wherein, X represents a reactive functional group having an epoxy group and R_2 represents an alkyl group having 1 to 10 carbon atoms)

in the range that the alkoxy group equivalent in the alkoxysilane compound (a) is 1.5 to 200 equivalents relative to 1 equivalent of the silanol group in the silanol-terminal silicone oil (b) and in the presence of a catalyst for condensation to form an alkoxysilane modified form(d), and then by, as a second step reaction, adding water to the resulting reaction liquid for hydrolysis· condensation of alkoxy groups in both the above alkoxysilane modified form (d) and the alkoxysilane (a) in the coexistence of alkoxysilane (a) under the reaction condensations performed at 50 to 150 °C for 5 to 30 hours.

14. The method for producing a reactive functional group-containing block-type-siloxane compound according to Claim 13, wherein m is 2 to 200.

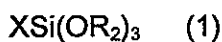
15. A method for producing a reactive functional group-containing block-type-siloxane compound which is a block-type siloxane oligomer having a chain silicone segment and a hydrolysis condensation segment of tri(C1-C10)alkoxysilane having a group selected from the group consisting of a reactive functional group having an epoxy group, a methyl group and a phenyl group, at least one of the hydrolysis condensation segments being a segment containing at least one reactive functional group having an epoxy group, which is characterized by, as a first step reaction, condensation reaction of

silanol-terminal silicone oil (b) represented by the general formula (2):



(wherein, plural existing R_3 may be the same or different from each other and each independently represents a straight chain, branched or cyclic alkyl group having 1 to 10 carbon atoms, an aryl group having 6 to 14 carbon atoms or an alkenyl group having 2 to 10 carbon atoms, and m represents 2 to 200 as an average value)

with an alkoxy silane compound (a) represented by the general formula (1):



(wherein, X represents a reactive functional group having an epoxy group and R_2 represents an alkyl group having 1 to 10 carbon atoms) and an alkoxy silane compound (c) represented by the general formula (3):



(wherein, R_4 represents a methyl group or a phenyl group, and R_2 may be the same or different from R_2 in the general formula (1) and each independently represents an alkyl group having 1 to 10 carbon atoms)

in the range that the total equivalent of the alkoxy group in the alkoxy silane compounds (a) and (c) is 1.5 to 200 equivalents relative to 1 equivalent of the silanol group in the silanol-terminal silicone oil (b) and in the presence of a catalyst for condensation to form an alkoxy silane modified form (d), and then by, as a second step reaction, adding water

to the resulting reaction product for hydrolysis- condensation of alkoxy groups in both the above alkoxysilane modified form (d) and the alkoxysilane (a) in the coexistence of alkoxysilane (a) under the reaction condensations performed at 50 to 150 °C for 5 to 30 hours.

16. The method for producing a reactive functional group-containing- block-type siloxane compound according to any one of Claims 13 to 15 which is characterized by successively conducting the first step reaction and the second step reaction in one-pot as a production process.

17. The method for producing a reactive functional group-containing block-type-siloxane compound according to any one of Claims 13 to 16, wherein the alkoxysilane compound represented by the general formula (1) is beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane or beta-(3,4-epoxycyclohexyl)ethyltriethoxysilane.

18. The method for producing a reactive functional group-containing block-type-siloxane compound according to any one of Claims 13 to 17 wherein R_3 in the silanol-terminal silicone oil (b) represented by the general formula (2) may be the same or different from each other and each independently represents a methyl group or a phenyl group.

19. The method for producing a reactive functional group-containing block-type-siloxane compound according to any one of Claims 13 to 16 wherein the alkoxysilane compound represented by the general formula (3) is at least one kind selected from the group

consisting of methyltrimethoxysilane, phenyltrimethoxysilane, methyltriethoxysilane and phenyltriethoxysilane.

20. A curable resin composition, which is characterized by containing the reactive functional group-containing block-type-siloxane compound (A) according to any one of Claims 1 to 13 and a curing agent (B).

21. The curable resin composition according to Claim 20, which is characterized by further containing a curing accelerator (C).

22. A cured product for optical semiconductors, which is obtained by heat curing the curable resin composition according to Claim 19 or 20.

23. An optical semiconductor element, which is sealed with the cured product for optical semiconductors according to Claim 21.