(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 September 2014 (12.09.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/136805 A1

(51) International Patent Classification:
C08G 77/14 (2006.01) *H01L 23/29* (2006.01)
C08L 83/06 (2006.01)

(21) International Application Number:
PCT/JP2014/055529

(22) International Filing Date:
26 February 2014 (26.02.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2013-043001 5 March 2013 (05.03.2013) JP

(71) Applicant: **DOW CORNING TORAY CO., LTD.** [JP/JP]; 5-1, Otemachi 1-chome, Chiyoda-ku, Tokyo, 1000004 (JP).

(72) Inventors: **MORITA, Yoshitsugu**; c/o Dow Corning Toray Co., Ltd., 2-2, Chigusakaigan, Ichihara-shi, Chiba, 2990108 (JP). **AMAKO, Masaaki**; c/o Dow Corning Toray Co., Ltd., 2-2, Chigusakaigan, Ichihara-shi, Chiba, 2990108 (JP). **ONODERA, Satoshi**; c/o Dow Corning Toray Co., Ltd., 2-2, Chigusakaigan, Ichihara-shi, Chiba, 2990108 (JP).

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

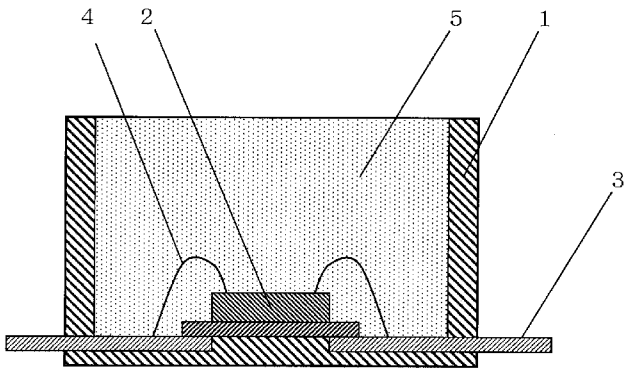
(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU,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

Published:

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

(54) **Title**: CURABLE SILICONE COMPOSITION, CURED PRODUCT THEREOF, AND OPTICAL SEMICONDUCTOR DEVICE

FIG. 1



(57) **Abstract**: The present invention relates to a curable silicone composition comprising: (A) an organopolysiloxane represented by the average unit formula: $(R^1R^2SiO_{2/2})_a(R^3SiO_{3/2})_b(XO_{1/2})_c$, wherein $R^1$is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, or a phenyl group; R^2 is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, a phenyl group, or an epoxy group-containing organic group, provided that at least one R^2 in a molecule is the epoxy group-containing organic group; R^3 is a condensed polycyclic aromatic group or a condensed polycyclic aromatic group-containing organic group; X is an alkyl group having from 1 to 3 carbon atoms or a hydrogen atom, *a* is a number from 0.20 to 0.60, *b* is a number from 0.40 to 0.80, a sum of *a* and *b* is 1.00, and *c* is a number from 0 to 0.5; (B) a curing agent; and (C) a curing accelerator. The curable silicone composition forms a cured product having a high refractive index and an adequate elastic modulus.

WO 2014/136805 A1

DESCRIPTION

CURABLE SILICONE COMPOSITION, CURED PRODUCT THEREOF, AND OPTICAL SEMICONDUCTOR DEVICE

Technical Field

[0001] The present invention relates to a curable silicone composition, a cured product thereof, and an optical semiconductor device.

[0002] Priority is claimed on Japanese Patent Application No. 2013-043001, filed on March 5, 2013, the content of which is incorporated herein by reference.

Background Art

[0003] Curable silicone compositions are used as sealing agents for LEDs, raw materials for lenses, and the like due to their excellence in transparency and heat resistance. Organopolysiloxanes, which are the main component of the curable silicone composition, comprise any combination of siloxane units (M units) represented by the general formula: $R_3SiO_{1/2}$, siloxane units (D units) represented by the general formula: $R_2SiO_{2/2}$, siloxane units (T units) represented by the general formula: $RSiO_{3/2}$, and siloxane units (Q units) represented by the formula: $SiO_{4/2}$ (in the formulas, R are the same or different monovalent hydrocarbon groups). To increase the high refractive index of an organopolysiloxane even higher, it is known that a condensed polycyclic aromatic group such as a naphthyl group or a condensed polycyclic aromatic group-containing organic group such as a naphthyl ethyl group is introduced as an organic group in the molecular chain. It is also known that an epoxy group-containing organic group is introduced as another organic functional group (see Patent Documents 1 and 2).

[0004] For example, Patent Document 1 discloses hydrolyzing and condensation reacting di(1-naphthyl)dimethoxysilane or 1-naphthyl methyldimethoxysilane, and 3-glycidoxypropyl trimethoxysilane or 3-glycidoxypropyl methyldimethoxysilane. In addition, Patent Document 2 discloses hydrolyzing and condensation reacting 9-phenanthrene triethoxysilane, 3-glycidoxypropyl trimethoxysilane, and methyl triethoxysilane, and hydrolyzing and condensation reacting 1-naphthyl triethoxysilane, 3-glycidoxypropyl trimethoxysilane, and triethoxysilane.

[0005] However, the organopolysiloxane prepared in Patent Document 1 contains a condensed polycyclic aromatic group such as a naphthyl group in a D unit, and an epoxy group-containing organic group in another D unit or in a T unit. Such an

organopolysiloxane has a large degree of molecular weight dispersity, and there is a problem that a cured product obtained by curing this organopolysiloxane has significantly low elastic modulus.

[0006] On the other hand, the organopolysiloxane prepared in Patent Document 2 contains a condensed polycyclic aromatic group such as a naphthyl group in a T unit, and an epoxy group-containing organic group in another T unit. Although such an organopolysiloxane has a small degree of molecular weight dispersity, there is a problem that a cured product obtained by curing this organopolysiloxane has significantly high elastic modulus.

Prior Art Documents

Patent Documents

[0007]

Patent Document 1: Japanese Unexamined Patent Application Publication No. 2010-007057A

Patent Document 2: Japanese Unexamined Patent Application Publication (Translation of PCT Application) No. 2011-504958A

Summary of Invention

Technical Problem

[0008] An object of the present invention is to provide a curable silicone composition that forms a cured product that is transparent and has a high refractive index and an adequate elastic modulus. Another object of the present invention is to provide a cured product that is transparent and has a high refractive index and an adequate elastic modulus. Yet another object of the present invention is to provide an optical semiconductor device with excellent reliability.

Solution to Problem

[0009] The curable silicone composition of the present invention comprises:

(A) an organopolysiloxane represented by the following average unit formula:

$$(R^1R^2SiO_{2/2})_a(R^3SiO_{3/2})_b(XO_{1/2})_c$$

wherein R^1 is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, or a phenyl group; R^2 is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, a phenyl group, or an epoxy group-containing organic group, provided that at least one R^2 in a molecule is the

epoxy group-containing organic group; R^3 is a condensed polycyclic aromatic group or a condensed polycyclic aromatic group-containing organic group; X is an alkyl group having from 1 to 3 carbon atoms or a hydrogen atom; **a** is a number from 0.20 to 0.60, **b** is a number from 0.40 to 0.80, a sum of **a** and **b** is 1.00, and **c** is a number from 0 to 0.5;

(B) a curing agent; and

(C) a curing accelerator.

[0010] In the formula for component (A), the epoxy group-containing organic group for R^2 is preferably a glycidoxyalkyl group, an epoxycyclohexyl alkyl group, or an oxiranylalkyl group, and R^3 is preferably a naphthyl group or a naphthyl ethyl group. Furthermore, relative to all of R^1 and R^2 in a molecule, at least 10 mol% is preferably epoxy group-containing organic groups.

[0011] In addition, the cured product of the present invention is produced by curing the composition described above.

[0012] Furthermore, the optical semiconductor device of the present invention is formed by covering or sealing an optical semiconductor element with the composition described above.

Effects of Invention

[0013] The curable silicone composition of the present invention is characterized by forming a cured product that is transparent and has a high refractive index and an adequate elastic modulus. Also, the cured product of the present invention is characterized by being transparent and having a high refractive index and an adequate elastic modulus. Furthermore, the optical semiconductor device of the present invention is characterized by having excellent reliability.

Brief Description of the Drawings

[0014]

FIG. 1 is a cross-sectional view of an LED that is an example of an optical semiconductor device of the present invention.

FIG. 2 is a cross-sectional view of a lens that is an example of a cured product of the present invention.

Detailed Description of the Invention

[0015] First, the curable silicone composition of the present invention will be described in detail.

[0016] Component (A) is an organopolysiloxane represented by the following average unit formula:

$$(R^1R^2SiO_{2/2})_a(R^3SiO_{3/2})_b(XO_{1/2})_c.$$

[0017] In the formula, R^1 is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, or a phenyl group. Examples of the alkyl group for R^1 include a methyl group, an ethyl group, a propyl group, a butyl group, a cyclohexyl group, a cyclopentyl group, and a cyclooctyl group. Of these, a methyl group is preferable. Examples of the alkenyl group for R^1 include a vinyl group, an allyl group, and a butenyl group. Of these, a vinyl group is preferable.

[0018] In the formula, R^2 is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, a phenyl group, or an epoxy group-containing organic group. Examples of the alkyl group for R^2 include the same groups described for R^1. Of these, a methyl group is preferable. Examples of the alkenyl group for R^2 include the same groups described for R^1. Of these, a vinyl group is preferable. Examples of the epoxy group-containing organic group for R^2 include glycidoxyalkyl groups such as a 2-glycidoxyethyl group, a 3-glycidoxypropyl group, and a 4-glycidoxybutyl group; epoxycycloalkylalkyl groups such as a 2-(3,4-epoxycyclohexyl) ethyl group, a 3-(3,4-epoxycyclohexyl)propyl group, a 2-(3,4-epoxynorbornyl)ethyl group, and a 2-(3,4-epoxy-3-methylcyclohexyl)-2-methylethyl group; and oxiranylalkyl groups such as a 4-oxiranylbutyl group and an 8-oxiranyloctyl group. Of these, a glycidoxyalkyl group is preferable, and a 3-glycidoxypropyl group is particularly preferable. Note that, in a molecule, at least one, or preferably at least two, R^2 are epoxy group-containing organic groups. In particular, because the curability of the curable silicone composition of the present invention is good, in component (A), the proportion of the epoxy group-containing organic groups relative to all of R^1 and R^2 in a molecule is preferably at least 10 mol%, and more preferably at least 15 mol%.

[0019] In the formula, R^3 is a condensed polycyclic aromatic group or a condensed polycyclic aromatic group-containing organic group. Examples of the condensed polycyclic aromatic group for R^3 include a naphthyl group, an anthracenyl group, a phenanthryl group, a pyrenyl group, and such condensed polycyclic aromatic groups where a hydrogen atom is replaced by an alkyl group such as a methyl group or an ethyl group; by an alkoxy group such as a methoxy group or an ethoxy group; or by a halogen atom such as a chlorine atom or a bromine atom. Of these, a naphthyl group is preferable.

Examples of the condensed polycyclic aromatic group-containing organic group for R^3 include condensed polycyclic aromatic group-containing alkyl groups such as a naphthyl ethyl group, a naphthyl propyl group, an anthracenyl ethyl group, a phenanthryl ethyl group, and a pyrenyl ethyl group; and such condensed polycyclic aromatic groups where a hydrogen atom is replaced by an alkyl group such as a methyl group or an ethyl group; by an alkoxy group such as a methoxy group or an ethoxy group; or by a halogen atom such as a chlorine atom or a bromine atom. The condensed polycyclic aromatic group-containing organic group for R^3 is preferably the condensed polycyclic aromatic group-containing alkyl groups, and particularly preferably a naphthyl ethyl group. An organopolysiloxane containing a condensed polycyclic aromatic group-containing alkyl group as R^3 has relatively low viscosity, and thus the viscosity of the present composition can be lowered.

[0020] In the formula, X is an alkyl group having from 1 to 3 carbon atoms or a hydrogen atom. Examples of the alkyl group for X include a methyl group, an ethyl group, and a propyl group. Of these, a methyl group is preferable.

[0021] In the formula, **a** indicates a proportion of D units and is a number from 0.20 to 0.60, and **b** indicates a proportion of T units and is a number from 0.40 to 0.80. Note that the sum of **a** and **b** is 1.00. This is because, when the value of **a** is greater than or equal to the lower limit of the range described above, the cured product obtained by curing the present composition will exhibit a good elastic modulus, and when the value of **a** is less than or equal to the upper limit of the range described above, the cured product obtained by curing the present composition will exhibit a high refractive index.

[0022] In the formula, **c** indicates a proportion of a unit represented by the formula: $XO_{1/2}$ that is formed in the course of manufacturing component (A), and is a number from 0 to 0.5. This is because when the value of **c** is less than or equal to the upper limit of the range described above, stability of component (A) itself will be enhanced. The above units are preferably contained in the present composition because the adhesive properties of the present composition will be enhanced, and/or the bonding properties toward substrates of the cured product obtained by curing the present composition will be enhanced.

[0023] The molecular weight of component (A) is not particularly limited, but from the perspectives of excellent handling/workability and the like of the present composition, the weight average molecular weight in terms of standard polystyrene, as measured by gel

permeation chromatography, is preferably in a range of 400 to 5,000, more preferably in a range of 500 to 3,000, and particularly preferably in a range of 1,000 to 2,000. A form of component (A) at 25°C is not particularly limited, and examples of the form include oil-like, paste-like, resin-like, gum-like, and solid (powder).

[0024] Furthermore, the refractive index at 25°C and at a wavelength of 632.8 nm of component (A) is preferably greater than or equal to 1.50, and particularly preferably greater than or equal to 1.53.

[0025] The method for manufacturing such an organopolysiloxane for component (A) is a method comprising a step of, in the presence of an acid or an alkali, hydrolyzing and condensation reacting:

a silane compound represented by the following general formula (I):

$$R^1R^4SiY_2$$

wherein R^1 is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, or a phenyl group; R^4 is an epoxy group-containing organic group; and Y is a hydrolysable group; and/or

a siloxane compound represented by the following general formula (II):

$$HO(R^1R^4SiO)_mH$$

wherein R^1 and R^4 are synonymous with those described above, and **m** is an integer from 1 to 100; and

optionally, a silane compound represented by the following general formula (III):

$$R^1{}_2SiY_2$$

wherein R^1 and Y are synonymous with those described above; and/or

a siloxane compound represented by the following general formula (IV):

$$HO(R^1{}_2SiO)_nH$$

wherein R^1 is synonymous with those described above, and **n** is an integer from 1 to 100; with a silane compound represented by the following general formula (V):

$$R^3SiY_3$$

wherein R^3 is a condensed polycyclic aromatic group or a condensed polycyclic aromatic group-containing organic group, and Y is synonymous with those described above.

[0026] The silane compound represented by the following general formula (I):

$$R^1R^4SiY_2$$

is a raw material for introducing a D unit having an epoxy group-containing organic group to the organopolysiloxane for component (A).

[0027] In the formula, R^1 is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, or a phenyl group, and examples thereof are synonymous with the groups described above. Of these, a methyl group is preferable.

[0028] In the formula, R^4 is an epoxy group-containing organic group, and examples thereof include glycidoxyalkyl groups such as a 2-glycidoxyethyl group, a 3-glycidoxypropyl group, and a 4-glycidoxybutyl group; epoxycycloalkylalkyl groups such as a 2-(3,4-epoxycyclohexyl)ethyl group, a 3-(3,4-epoxycyclohexyl)propyl group, a 2-(3,4-epoxynorbornyl)ethyl group, and a 2-(3,4-epoxy-3-methylcyclohexyl)-2-methylethyl group; and oxiranylalkyl groups such as a 4-oxiranylbutyl group and an 8-oxiranyloctyl group. Of these, a glycidoxyalkyl group is preferable, and a 3-glycidoxypropyl group is particularly preferable.

[0029] In the formula, Y is a hydrolysable group, and examples thereof include an alkoxy group, an acyloxy group, and a halogen atom. Examples of the alkoxy group for Y include a methoxy group, an ethoxy group, and a propoxy group. Examples of the acyloxy group for Y include an acetoxy group. Examples of the halogen atom for Y include a chlorine atom and a bromine atom.

[0030] Examples of such a silane compound include 3-glycidoxypropyl methyldimethoxysilane, 3-glycidoxypropyl methyldiethoxysilane, 3-glycidoxypropyl ethyldimethoxysilane, 2-(3,4-epoxycyclohexyl)ethylmethyldimethoxysilane, 2-(3,4-epoxycyclohexyl)ethylmethyldiethoxysilane, 4-oxiranylbutyl methyldimethoxysilane, 8-oxiranyloctyl methyldimethoxysilane, 3-glycidoxypropyl methyldiacetoxysilane, 3-glycidoxypropyl ethyldiacetoxysilane, 2-(3,4-epoxycyclohexyl)ethylmethyl diacetoxysilane, 3-glycidoxypropyl methyldichlorosilane, 3-glycidoxypropyl ethyldichlorosilane, and 2-(3,4-epoxycyclohexyl)ethylmethyl dichlorosilane.

[0031] The siloxane compound represented by the following general formula (II):

$$HO(R^1R^4SiO)_mH$$

is also a raw material for introducing a D unit having an epoxy group-containing organic group to the organopolysiloxane for component (A).

[0032] In the formula, R^1 is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, or a phenyl group, and examples thereof are synonymous with the groups described above. Of these, a methyl group is preferable.

Also, in the formula, R^4 is an epoxy group-containing organic group, and examples thereof are synonymous with the groups described above. Of these, a glycidoxyalkyl group is preferable, and particularly a 3-glycidoxypropyl group is preferable. Also, in the formula, **m** is an integer from 1 to 100, preferably an integer from 1 to 50, and particularly preferably an integer from 1 to 20.

[0033] The silane compound represented by the following general formula (III):

$R^1_2SiY_2$

is an optional raw material for introducing a D unit that is free of an epoxy group-containing organic group to the organopolysiloxane for component (A).

[0034] In the formula, R^1 is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, or a phenyl group, and examples thereof are synonymous with the groups described above. Of these, a methyl group is preferable. Also, Y is a hydrolysable group, and examples thereof are synonymous with the groups described above.

[0035] Examples of such a silane compound include dimethyldimethoxysilane, dimethyldiethoxysilane, methylphenyldimethoxysilane, methylphenyldiethoxysilane, methylethyldimethoxysilane, ethylphenyldimethoxysilane, diphenyldimethoxysilane, diphenyldiethoxysilane, dimethyldiacetoxysilane, methylphenyldiacetoxysilane, ethylphenyldiacetoxysilane, diphenyldiacetoxysilane, dimethyldichlorosilane, methylphenyldichlorosilane, and diphenyldichlorosilane.

[0036] The siloxane compound represented by the following general formula (IV):

$HO(R^1_2SiO)_nH$

is also an optional raw material for introducing a D unit that is free of an epoxy group-containing organic group to the organopolysiloxane for component (A).

[0037] In the formula, R^1 is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, or a phenyl group, and examples thereof are synonymous with the groups described above. Of these, a methyl group is preferable. Also, in the formula, **n** is an integer from 1 to 100, preferably an integer from 1 to 50, and particularly preferably an integer from 1 to 20.

[0038] The silane compound represented by the following general formula (V):

R^3SiY_3

is a raw material for introducing a T unit having a condensed polycyclic aromatic group or a condensed polycyclic aromatic group-containing organic group to the organopolysiloxane for component (A).

[0039] In the formula, R^3 is a condensed polycyclic aromatic group or a condensed polycyclic aromatic group-containing organic group, and examples thereof are synonymous with the groups described above. Of these, a naphthyl group and a naphthyl ethyl group are preferable. Also, in the formula, Y is a hydrolysable group, and examples thereof are synonymous with the groups described above.

[0040] Examples of such a silane compound include naphthyltrimethoxysilane, anthracenyl trimethoxysilane, phenanthryl trimethoxysilane, pyrenyl trimethoxysilane, naphthyl triethoxysilane, anthracenyl triethoxysilane, phenanthryl triethoxysilane, pyrenyl triethoxysilane, naphthyl ethyl trimethoxysilane, naphthyl propyl trimethoxysilane, anthracenyl ethyl trimethoxysilane, naphthyl triacetoxysilane, anthracenyl triacetoxysilane, phenanthryl triacetoxysilane, pyrenyl triacetoxysilane, naphthyl trichlorosilane, anthracenyl trichlorosilane, phenanthryl trichlorosilane, and pyrenyl trichlorosilane.

[0041] The manufacturing method described above is characterized by, in the presence of an acid or an alkali, hydrolyzing and condensation reacting the silane compound represented by the general formula (I) and/or the siloxane compound represented by the general formula (II), and optionally, the silane compound represented by the general formula (III) and/or the siloxane compound represented by the general formula (IV), with the silane compound represented by the general formula (V).

[0042] In the manufacturing method described above, the compounding amount of each of the raw materials is such that the proportion of the D unit introduced to the organopolysiloxane for component (A) (by using the silane compound represented by the general formula (I) and/or the siloxane compound represented by the general formula (II), and optionally, the silane compound represented by the general formula (III) and/or the siloxane compound represented by the general formula (IV) as raw materials) will be a number from 0.20 to 0.60, and that the proportion of the T unit introduced to the resulting organopolysiloxane for component (A) (by using the silane compound represented by the general formula (V) as a raw material) will be a number from 0.40 to 0.80.

[0043] Furthermore, the proportion of the silane compound represented by the general formula (I) or the siloxane compound represented by the general formula (II), and the optionally used silane compound represented by the general formula (III) or siloxane

compound represented by the general formula (IV), for introducing the siloxane of the D unit, is not particularly limited. However, from the perspective of the curability of the present composition being good, the proportion of these compounds are at an amount where the proportion of R^4 to all of R^1 and R^4 will be preferably at least 10 mol%, and more preferably will be at least 15 mol%.

[0044] Examples of the acid that can be used in the manufacturing method described above include hydrochloric acid, acetic acid, formic acid, nitric acid, oxalic acid, sulfuric acid, phosphoric acid, polyphosphoric acid, polycarboxylic acid, trifluoromethane sulfonic acid, and ion exchange resins. Furthermore, examples of the alkali that can be used in the manufacturing method described above include inorganic alkalis such as potassium hydroxide and sodium hydroxide; and organic base compounds such as triethylamine, diethylamine, monoethanolamine, diethanolamine, triethanolamine, ammonia water, tetramethylammonium hydroxide, alkoxysilanes having an amino group, and aminopropyltrimethoxysilane.

[0045] In the manufacturing method described above, an organic solvent may be used. Examples of the organic solvent include ethers, ketones, acetates, aromatic or aliphatic hydrocarbons, and 3-butyrolactone; and mixtures of two or more types of such solvents. Specifically, the organic solvents are exemplified by propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether, propylene glycol monopropyl ether, propylene glycol monobutyl ether, propylene glycol mono-t-butyl ether, 3-butyrolactone, toluene, and xylene.

[0046] In order to accelerate the hydrolysis and condensation reaction of each of the components in the manufacturing method described above, water or a mixed solution of water and an alcohol is preferably added. Preferred examples of the alcohol include methanol and ethanol. If an organic solvent is used and this reaction is accelerated by heating, the reaction is preferably performed at the reflux temperature of the organic solvent.

[0047] Component (B) is a curing agent of the present composition, and the curing agent is not particularly limited as long as the curing agent reacts with an epoxy group in component (A) to cure the present composition. Examples of component (B) include phenol resins such as bisphenol A, bisphenol F, bisphenol AD, bisphenol S, tetramethyl bisphenol A, tetramethyl bisphenol F, tetramethyl bisphenol AD, tetramethyl bisphenol S, tetrabromo bisphenol A, tetrachloro bisphenol A, tetrafluoro bisphenol A, biphenol,

dihydroxynaphthalene, 1,1,1-tris(4-hydroxyphenyl)methane, 4,4-(1-(4-(1-(4-hydroxyphenyl)-1-methylethyl)phenyl)ethylidene)bisphenol, phenol novolac, cresol novolac, bisphenol A novolac, bromophenol novolac, and bromo bisphenol A novolac; polyols that have hydrogenated aromatic rings of these phenol resins; alicyclic acid anhydrides such as polyazelaic anhydride, methyltetrahydrophthalic anhydride, tetrahydrophthalic anhydride, methylhexahydrophthalic anhydride, hexahydrophthalic anhydride, 5-norbornen-2,3-dicarboxylic acid anhydride, norbornan-2,3-dicarboxylic acid anhydride, methyl-5-norbornen-2,3-dicarboxylic acid anhydride, methyl-norbornan-2,3-dicarboxylic acid anhydride, cyclohexan-1,2,3-tricarboxylic acid-1,2 anhydride, and cyclohexan-1,2,4-tricarboxylic acid-1,2 anhydride; alkyl-substituted glutaric acid anhydrides such as 3-alkyl glutaric acid anhydride that may be branched and contains an alkyl group having from 1 to 8 carbon atoms (e.g. 3-methyl glutaric acid anhydride), 2,3-dialkyl glutaric acid anhydride that may be branched and contains an alkyl group having from 1 to 8 carbons (e.g. 2-ethyl-3-propyl glutaric acid anhydride), and 2,4-dialkyl glutaric acid anhydride that may be branched and contains an alkyl group having from 1 to 8 carbon atoms (e.g. 2,4-diethyl glutaric acid anhydride and 2,4-dimethyl glutaric acid anhydride); aromatic acid anhydrides such as phthalic anhydride, trimellitic anhydride, and pyromellitic anhydride; and a mixture of two or more of these. In particular, component (B) is preferably an acid anhydride such as alicyclic acid anhydride, alkyl-substituted glutaric acid anhydride, or aromatic acid anhydride; more preferably alicyclic acid anhydride or alkyl-substituted glutaric acid anhydride; and particularly preferably methylhexahydrophthalic anhydride, hexahydrophthalic anhydride, norbornan-2,3-dicarboxylic acid anhydride, methyl-norbornan-2,3-dicarboxylic acid anhydride, cyclohexane-1,2,3-tricarboxylic acid-1,2 anhydride, cyclohexane-1,2,4-tricarboxylic acid-1,2 anhydride, or 2,4-diethyl glutaric acid anhydride. When the acid anhydride-based curing agent is used as component (B), the refractive index of the cured product obtained by curing the present composition will be easily controlled.

[0048] Although the content of component (B) is not particularly limited, the content is preferably greater than or equal to 1 part by weight, more preferably greater than or equal to 5 parts by weight, and particularly preferably greater than or equal to 20 parts by weight, while the content is preferably less than or equal to 200 parts by weight, and particularly preferably less than or equal to 160 parts by weight, per 100 parts by weight of component (A), due to the capability of sufficiently curing the present composition,

imparting the cured product obtained by curing the present composition excellent heat resistance and light resistance, and lowering the moisture permeability of the cured product.

[0049] Component (C) is a curing accelerator for accelerating the curing of the present composition. Examples of component (C) include aliphatic amines such as ethylene diamine, triethylene pentamine, hexamethylene diamine, dimer acid-modified ethylenediamine, N-ethylamino piperazine, and isophoronediamine; aromatic amines such as m-phenylenediamine, p-phenylenediamine, 3,3'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenylmethane, and 4,4'-diaminodiphenylether; imidazoles such as 2-methylimidazole, 2-ethyl-4-methylimidazole, 2-phenylimidazole, and 2-phenyl-4-methylimidazole; tertiary amines such as dimethyl benzylamine 1,8-diazabicyclo[5,4,0]undec-7-ene, and the salts thereof; phosphines such as triphenylphosphine; phosphonium salts such as triphenyl phosphonium bromide and methyltributyl phosphonium dimethylphosphate; aminotriazole; tin compounds such as tin octylate and dibutyltin dilaurate; zinc compounds such as zinc octylate; and acetyl acetonates of metals such as aluminum, chromium, cobalt, and zirconium; and a mixture of two or more of these.

[0050] Although the content of component (C) is not particularly limited, the content is preferably greater than or equal to 0.01 parts by weight, and particularly preferably greater than or equal to 0.1 parts by weight, while the content is preferably less than or equal to 5 parts by weight, per 100 parts by weight of component (A), from the perspectives of sufficiently accelerating curing of the present composition, suppressing coloration of the cured product obtained by curing the present composition, and imparting excellent heat resistance and light resistance to the cured product.

[0051] Furthermore, from the perspective of enhancing the light resistance and heat resistance of the resulting cured product, epoxy compounds such as 3',4'-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, bis(3,4-epoxycyclohexylmethyl)adipate, vinylcyclohexene dioxide, and hydrogenated bisphenol A diglycidylether may be compounded in the present composition.

[0052] Although the content of the epoxy compound is not particularly limited, the content is preferably less than or equal to 200 parts by weight, and particularly preferably less than or equal to 100 parts by weight, per 100 parts by weight of component (A).

[0053] The present composition may further contain an antioxidant from the perspective of being able to suppress coloration of the cured product even when the cured product is exposed to a high temperature environment for a long time. As the antioxidant, known antioxidants including hindered phenol type antioxidants such as 2,6-tert-butyl-p-cresol, butylated hydroxyanisole, 2,6-tert-butyl-p-ethylphenol, stearyl-β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 2,2-methylene bis(4-methyl-6-tert-butylphenol), 2,2-methylene bis(4-ethyl-6-tert-butylphenol), 4,4'-thiobis(3-methyl-6-tert-butylphenol), 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, and tetrakis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]methane; thioether compound type antioxidants such as dilauryl 3,3'-thiodipropionate, dimyristyl 3,3'-thiodipropionate, distearyl 3,3'-thiodipropionate, and pentaerythrityltetrakis(3-laurylthiopropionate); phosphorus atom-containing antioxidants such as triphenylphosphate, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, 10-(3,5-di-tert-butyl 4-hydroxybenzyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, and 10-decyloxy-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide; and the like can be used alone or in a combination of two or more.

[0054] Although the content of the antioxidant is not particularly limited, the content is preferably greater than or equal to 0.01 parts by weight, and particularly preferably greater than or equal to 0.05 parts by weight, while the content is preferably less than or equal to 10.0 parts by weight, and particularly preferably less than or equal to 5.0 parts by weight, per 100 parts by weight of the component (A), from the perspectives of sufficiently suppressing coloration of the cured product and not lowering the light resistance of the cured product even when the cured product is exposed to a high temperature environment for a long time.

[0055] When the present composition is used as a sealing agent for an optical semiconductor element, from the perspectives of increasing the refractive index of the cured product and imparting excellent light extraction properties to optical semiconductor elements such as LEDs, the present composition preferably comprises microparticles containing a metal element such as Al, In, Ge, Sn, Ti, Zr, and Hf. In particular, from the perspectives of excellence in enhancing the refractive index and excellence in optical transparency, the microparticles are preferably microparticles containing Zr. The content of the metal element in the microparticle is not particularly limited; however, to sufficiently enhance the refractive index of the cured product, 80% or more of all metal

elements present in the microparticle are preferably the metal elements described above. The refractive index of this microparticle is preferably 1.50 or greater. Also, although the average primary particle diameter of this microparticle is not particularly limited, from the perspectives of being able to suppress white turbidness of the present composition and to suppress light scattering of the cured product, the average primary particle diameter is preferably less than or equal to 20 nm, and particularly preferably less than or equal to 15 nm, while the average primary particle diameter is preferably greater than or equal to 3 nm.

[0056] Although the content of the microparticles are not particularly limited, from the perspectives of enhancing the refractive index of the cured product obtained by curing the present composition and not deteriorating the handling/workability of the present composition, the content is preferably greater than or equal to 1 part by weight, and particularly preferably greater than or equal to 5 parts by weight, while the content is preferably less than or equal to 100 parts by weight, and particularly preferably less than or equal to 80 parts by weight, per 100 parts by weight of component (A).

[0057] The present composition may contain a coupling agent for enhancing the adhesion of the composition. Examples of the coupling agent include silane coupling agents such as vinyl triethoxysilane, vinyl trimethoxysilane, 3-glycidoxypropyl trimethoxysilane, γ-methacryloxypropyl trimethoxysilane, γ-aminopropyl trimethoxysilane, N-phenyl-3-aminopropyl trimethoxysilane; and a mixture of two or more of these coupling agents.

[0058] Although the content of the coupling agent is not particularly limited, from the perspectives of enhancing the adhesion of the present composition and suppressing the shrinkage of the resulting cured product, the content is preferably greater than or equal to 0.1 parts by weight while the content is preferably less than or equal to 5 parts by weight, per 100 parts by weight of component (A).

[0059] In addition, the present composition may contain silica fine powder, a high molecular weight silicone resin, or the like to adjust the viscosity of the present composition. In particular, because the silica fine powder works not only as a thickener but also as a thixotropy imparting agent, the silica fine powder exhibits effects such as controlling the fluidity of the present composition and/or preventing the precipitation of fluorescent substances, and the like. Although the average particle diameter of the silica fine powder is not particularly limited, from the perspective of not losing the transparency of the present composition, the average particle diameter is preferably less than or equal to

100 nm. Also, because the silica fine powder has sufficient thickening effect and thixotropy imparting effect, and because agglutination of the silica fine powder does not increase too much, and dispersibility of the silica fine powder is good, the BET specific surface area of the silica fine powder is preferably in a range from 30 m^2/g to 500 m^2/g.

[0060] The present composition may contain a diluent to improve the workability by reducing the viscosity of the present composition. Examples of the diluent include glycerin diglycidyl ether, butanediol diglycidyl ether, neopentylglycol glycidyl ether, cyclohexane dimethanol diglycidyl ether, alkylene diglycidyl ether, polyglycol diglycidyl ether, polypropylene glycol diglycidyl ether, trimethylolpropane triglycidyl ether, glycerin triglycidyl ether, 4-vinylcyclohexene monoxide, vinylcyclohexene dioxide, methylated vinylcyclohexene dioxide, diglycidyl aniline, and a mixture of two or more of these.

[0061] The present composition may optionally contain additives such as an anti-foaming agent, a coloring agent, a fluorescent substance, a modifying agent, a leveling agent, a light diffusing agent, a thermally conductive filler, and a flame retardant.

[0062] The preparation method of the present composition is not particularly limited, and examples include mixing, at room temperature or while heating, by using a mixer such as a homo-disper, homomixer, universal mixer, planetary mixer, kneader, three roll mill, or a bead mill.

[0063] The cured product of the present invention will now be described in detail.

[0064] The cured product of the present invention is formed by curing the curable silicone composition described above. The shape of the cured product of the present invention is not particularly limited, and examples include a sheet-shape, a film-shape, a convex lens shape, a concave lens shape, a Fresnel lens shape, a truncated cone shape, and a square cone platform. The cured product of the present invention can be handled alone or in a state in which it covers, seals, or adheres an optical semiconductor element or the like. A cross-sectional drawing of a lens that is an example of a cured product of the present invention is illustrated in FIG. 2.

[0065] The cured product of the present invention is transparent and has a high refractive index and an adequate elastic modulus. Although the elastic modulus of the cured product is not particularly limited, for example, the storage elastic modulus is preferably in a range of 1 to 50 MPa. Also, the refractive index of the cured product is not particularly limited; however, the refractive index at a wavelength of 632.8 nm of the cured product at 25°C is preferably greater than or equal to 1.5.

[0066] To manufacture the cured product of the present invention, compression molding, transfer molding, injection molding, casting, dipping, powder molding, or the like can be used. When using these methods, the heating temperature is generally in a range from 100°C to 250°C, and the molding time is from several tens of seconds to several minutes. After the molding, it is preferable to further heat the resulting product for 30 minutes to 20 hours.

[0067] The optical semiconductor device of the present invention will now be explained in detail.

[0068] The optical semiconductor device of the present invention is characterized in that an optical semiconductor element is covered or sealed by a cured product of the curable silicone composition described above. An example of this optical semiconductor element is a light emitting diode (LED) chip. Examples of such an optical semiconductor device include a light emitting diode (LED), a photocoupler, and a CCD.

[0069] FIG. 1 illustrates a cross-sectional view of a single surface mounted type LED, which is one example of the optical semiconductor device of the present invention. In the LED illustrated in FIG. 1, an LED chip 1 is die-bonded to a lead frame 2, and the LED chip 1 and a lead frame 3 are wire-bonded by a bonding wire 4. This LED chip 1 is covered by a cured product 5 of the curable silicone composition of the present invention.

[0070] An example of a method of producing the surface mounted type LED illustrated in FIG. 1 is a method of die-bonding the LED chip 1 to the lead frame 2, wire-bonding the LED chip 1 and the lead frame 3 with a gold bonding wire 4, coating the LED chip 1 with the curable silicone composition of the present invention, and then curing the composition by heating at 50 to 200°C.

Examples

[0071] The curable silicone composition, the cured product thereof, and the optical semiconductor device of the present invention will be described in detail hereinafter using examples. Moreover, Me in the formulas is a methyl group, Ph in the formulas is a phenyl group, Naph in the formulas is a 1-naphthyl group, and Ep in the formulas is a 3-glycidoxypropyl group. In addition, the characteristics of the organopolysiloxane were evaluated as follows.

[0072]

[Weight average molecular weight and dispersity]

The weight average molecular weight (Mw) and number average molecular weight (Mn) in terms of standard polystyrene of the organopolysiloxane were determined by gel permeation chromatography using an RI detector. The dispersity (Mw/Mn) was determined from these values.

[0073]

[Refractive index]

The refractive index of the organopolysiloxane at 25°C was measured using an Abbe refractometer. As a light source, visible light (632.8 nm) was used.

[0074]

[Viscosity]

The viscosity at 25°C of the organopolysiloxane was measured using a rotational viscometer VG-DA (manufactured by Shibaura System Co., Ltd.).

[0075]

[Epoxy equivalent weight]

From the structure identified by an analysis using nuclear magnetic resonance spectroscopy, the epoxy equivalent weight (g/mol) of the organopolysiloxane was determined.

[0076]

[Methoxy group content]

From the structure identified by an analysis using nuclear magnetic resonance spectroscopy, the methoxy group content (% by weight) in the organopolysiloxane was determined.

[0077]

Additionally, the characteristics of the curable silicone composition and the cured product thereof were evaluated as follows.

[0078]

[Viscosity of the curable silicone composition]

The viscosity at 25°C of the curable silicone composition was measured using an AR 500 (manufactured by TA Instruments). Note that the viscosity was measured using a cone having a cone diameter of 20 mm, and a cone angle of 2° at 20 s^{-1}.

[0079]

[Storage elastic modulus of the cured product]

The curable silicone composition was heated for one hour at 150°C to produce a film-like cured product having a 0.5 mm thickness. Next, by using an MCR 301 Rheometer (manufactured by Anton Paar GmbH), the 0.5 mm thick film sample was sandwiched between parallel plates having diameters of 8 mm, and the storage elastic modulus value at 25°C was measured by applying the following conditions: strain: 0.1%; frequency: 1 Hz; normal force: constant pressure of 5 N; and the temperature was raised at a rate of 3°C/min from -10°C up to 50°C.

[0080]

[Refractive index of the cured product]

The refractive index at 25°C of the cured product prepared by the method described above was measured using a prism coupler method. A 632.8 nm laser light source was used for the measurement.

[0081]

[Transparency of the cured product]

The transparency of the cured product prepared by the method described above was confirmed visually.

[0082]

[Reference Example 1]

49.67 g of 1-naphthyltrimethoxysilane, 14.69 g of 3-glycidoxypropyl methyldimethoxysilane, and 47.49 g of toluene were placed in a reaction vessel provided with an agitator, a thermometer, a reflux tube, and a dropping funnel, and agitated. A mixture of 0.07 g of 50% potassium hydroxide aqueous solution, 9.90 g of water, and 9.90 g of methanol was gradually added to the reaction vessel using the dropping funnel. After the addition was completed, the mixture was refluxed for one hour. Produced methanol and excess water was removed via azeotropic dehydration and then the resulting product was reacted for eight hours in toluene at reflux. After cooling, the resulting product was neutralized using acetic acid. After the neutralized salt was filtered, toluene and low-boiling components were heated under reduced pressure to remove them by distillation. Thus, 47.00 g of transparent brown solid (at room temperature) was obtained.

[0083] The solid was confirmed, by an analysis using nuclear magnetic resonance spectroscopy, to be an organopolysiloxane represented by the following average unit formula:

$(EpMeSiO_{2/2})_{0.24}(NaphSiO_{3/2})_{0.76}(MeO_{1/2})_{0.05}$.

The epoxy equivalent weight of the organopolysiloxane was 740 g/mol. The methoxy group content of the organopolysiloxane was 0.8 % by weight. The weight average molecular weight (Mw) was 1,400. The dispersity (Mw/Mn) was 1.12. The refractive index was 1.615.

[0084]

[Reference Example 2]

37.25 g of 1-naphthyltrimethoxysilane, 33.05 g of 3-glycidoxypropyl methyldimethoxysilane, and 53.03 g of toluene were placed in a reaction vessel provided with an agitator, a thermometer, a reflux tube, and a dropping funnel, and agitated. A mixture of 0.07 g of 50% potassium hydroxide aqueous solution, 10.12 g of water, and 10.12 g of methanol was gradually added to the reaction vessel using the dropping funnel. After the addition was completed, the mixture was refluxed for one hour. Produced methanol and excess water was removed via azeotropic dehydration and then the resulting product was reacted for eight hours in toluene at reflux. After cooling, the resulting product was neutralized using acetic acid. After the neutralized salt was filtered, toluene and low-boiling components were heated under reduced pressure to remove them by distillation. Thus, 53.70 g of transparent brown gum-like substance (at room temperature) was obtained.

[0085] The substance was confirmed, by an analysis using nuclear magnetic resonance spectroscopy, to be an organopolysiloxane represented by the following average unit formula:

$(EpMeSiO_{2/2})_{0.50}(NaphSiO_{3/2})_{0.50}$.

The epoxy equivalent weight of the organopolysiloxane was 350 g/mol. Almost no methoxy group was observed, and the methoxy group content was less than 0.1 % by weight. The weight average molecular weight (Mw) was 1,800. The dispersity (Mw/Mn) was 1.20. The refractive index was 1.568.

[0086]

[Reference Example 3]

37.25 g of 1-naphthyltrimethoxysilane, 33.05 g of 3-glycidoxypropyl methyldimethoxysilane, and 58.22 g of toluene were placed in a reaction vessel provided with an agitator, a thermometer, a reflux tube, and a dropping funnel, and agitated. A mixture of 0.07 g of 50% potassium hydroxide aqueous solution, 4.73 g of water, and 4.73 g of methanol was gradually added to the reaction vessel using the dropping funnel. After

the addition was completed, the mixture was refluxed for one hour. Produced methanol and excess water was removed via azeotropic dehydration and then the resulting product was reacted for eight hours in toluene at reflux. After cooling, the resulting product was neutralized using acetic acid. After the neutralized salt was filtered, toluene and low-boiling components were heated under reduced pressure to remove them by distillation. Thus, 56.95 g of transparent yellow liquid with a viscosity at 25°C of 1,600 mPa•s was obtained.

[0087] The liquid was confirmed, by an analysis using nuclear magnetic resonance spectroscopy, to be an organopolysiloxane represented by the following average unit formula:

$(EpMeSiO_{2/2})_{0.49}(NaphSiO_{3/2})_{0.51}(MeO_{1/2})_{0.20}$.

The epoxy equivalent weight of the organopolysiloxane was 370 g/mol. The methoxy group content of the organopolysiloxane was 3.4 % by weight. The weight average molecular weight (Mw) was 1,200. The dispersity (Mw/Mn) was 1.26. The refractive index was 1.543.

[0088]

[Reference Example 4]

49.67 g of 1-naphthyltrimethoxysilane, 15.76 g of 3-glycidoxypropyl trimethoxysilane, and 47.03 g of toluene were placed in a reaction vessel provided with an agitator, a thermometer, a reflux tube, and a dropping funnel, and agitated. A mixture of 0.07 g of 50% potassium hydroxide aqueous solution, 10.80 g of water, and 10.80 g of methanol was gradually added to the reaction vessel using the dropping funnel. After the addition was completed, the mixture was refluxed for one hour. Produced methanol and excess water was removed via azeotropic dehydration and then the resulting product was reacted for eight hours in toluene at reflux. After cooling, the resulting product was neutralized using acetic acid. After the neutralized salt was filtered, toluene and low-boiling components were heated under reduced pressure to remove them by distillation. Thus, 56.95 g of transparent pale yellow powder (at room temperature) was obtained.

[0089] The powder was confirmed, by an analysis using nuclear magnetic resonance spectroscopy, to be an organopolysiloxane represented by the following average unit formula:

$(EpSiO_{3/2})_{0.24}(NaphSiO_{3/2})_{0.76}$.

The epoxy equivalent weight of the organopolysiloxane was 720 g/mol. Almost no methoxy group was observed, and the methoxy group content was less than 0.1 % by weight. The weight average molecular weight (Mw) was 2,200. The dispersity (Mw/Mn) was 1.37. The refractive index was 1.623.

[0090]

[Reference Example 5]

50.00 g of 1-naphthylmethyl dimethoxysilane, 50.85 g of 3-glycidoxypropyl trimethoxysilane, and 76.13 g of toluene were placed in a reaction vessel provided with an agitator, a thermometer, a reflux tube, and a dropping funnel, and agitated. A mixture of 0.07 g of cesium hydroxide monohydrate, 14.51 g of water, and 14.51 g of methanol was gradually added to the reaction vessel using the dropping funnel. After the addition was completed, the mixture was refluxed for one hour. Produced methanol and excess water was removed via azeotropic dehydration and then the resulting product was reacted for eight hours in toluene at reflux. After cooling, the resulting product was neutralized using acetic acid. After the neutralized salt was filtered, toluene and low-boiling components were heated under reduced pressure to remove them by distillation. Thus, 76.20 g of slightly yellow solid (at room temperature) was obtained.

[0091] The solid was confirmed, by an analysis using nuclear magnetic resonance spectroscopy, to be an organopolysiloxane represented by the following average unit formula:

$(NaphMeSiO_{2/2})_{0.49}(EpSiO_{3/2})_{0.51}$.

The epoxy equivalent weight of the organopolysiloxane was 350 g/mol. Almost no methoxy group was observed, and the methoxy group content was less than 0.1 % by weight. The weight average molecular weight (Mw) was 1,800. The dispersity (Mw/Mn) was 1.36. The refractive index was 1.569.

[0092]

[Reference Example 6]

50.00 g of 1-naphthylmethyl dimethoxysilane, 50.85 g of 3-glycidoxypropyl trimethoxysilane, and 3.54 g of dimethylpolysiloxane represented by the following formula:

$HO(Me_2SiO)_{10}H$,

and 79.65 g of toluene were placed in a reaction vessel provided with an agitator, a thermometer, a reflux tube, and a dropping funnel, and agitated. A mixture of 0.08 g of cesium hydroxide monohydrate, 14.51 g of water, and 14.51 g of methanol was gradually added to the reaction vessel using the dropping funnel. After the addition was completed, the mixture was refluxed for one hour. Produced methanol and excess water was removed via azeotropic dehydration and then the resulting product was reacted for eight hours in toluene at reflux. After cooling, the resulting product was neutralized using acetic acid. After the neutralized salt was filtered, toluene and low-boiling components were heated under reduced pressure to remove them by distillation. Thus, 79.22 g of slightly yellow solid (at room temperature) was obtained.

[0093] The solid was confirmed, by an analysis using nuclear magnetic resonance spectroscopy, to be an organopolysiloxane represented by the following average unit formula:

$$(NaphMeSiO_{2/2})_{0.45}(Me_2SiO_{2/2})_{0.10}(EpSiO_{3/2})_{0.45}(MeO_{1/2})_{0.01}.$$

The epoxy equivalent weight of the organopolysiloxane was 370 g/mol. Almost no methoxy group was observed, and the methoxy group content was less than 0.1 % by weight. The weight average molecular weight (Mw) was 1,700. The dispersity (Mw/Mn) was 1.41. The refractive index was 1.561.

[0094]

[Reference Example 7]

59.40 g of phenyltrimethoxysilane, 66.10 g of 3-glycidoxypropyl methyldimethoxysilane, and 91.00 g of toluene were placed in a reaction vessel provided with an agitator, a thermometer, a reflux tube, and a dropping funnel, and agitated. A mixture of 0.13 g of 50% potassium hydroxide aqueous solution, 20.25 g of water, and 20.25 g of methanol was gradually added to the reaction vessel using the dropping funnel. After the addition was completed, the mixture was refluxed for one hour. Produced methanol and excess water was removed via azeotropic dehydration and then the resulting product was reacted for eight hours in toluene at reflux. After cooling, the resulting product was neutralized using acetic acid. After the neutralized salt was filtered, toluene and low-boiling components were heated under reduced pressure to remove them by distillation. Thus, 90.80 g of transparent yellow liquid with a viscosity at 25°C of 13,400 mPa•s was obtained.

[0095] The liquid was confirmed, by an analysis using nuclear magnetic resonance spectroscopy, to be an organopolysiloxane represented by the following average unit formula:

$(EpMeSiO_{2/2})_{0.51}(PhSiO_{3/2})_{0.49}$.

The epoxy equivalent weight of the organopolysiloxane was 300 g/mol. Almost no methoxy group was observed, and the methoxy group content was less than 0.1 % by weight. The weight average molecular weight (Mw) was 2,600. The dispersity (Mw/Mn) was 1.34. The refractive index was 1.513.

[0096]

[Reference Example 8]

59.40 g of phenyltrimethoxysilane, 66.10 g of 3-glycidoxypropyl methyldimethoxysilane, and 101.35 g of toluene were placed in a reaction vessel provided with an agitator, a thermometer, a reflux tube, and a dropping funnel, and agitated. A mixture of 0.13 g of 50% potassium hydroxide aqueous solution, 9.45 g of water, and 9.45 g of methanol was gradually added to the reaction vessel using the dropping funnel. After the addition was completed, the mixture was refluxed for one hour. Produced methanol and excess water was removed via azeotropic dehydration and then the resulting product was reacted for eight hours in toluene at reflux. After cooling, the resulting product was neutralized using acetic acid. After the neutralized salt was filtered, toluene and low-boiling components were heated under reduced pressure to remove them by distillation. Thus, 99.35 g of transparent yellow liquid with a viscosity at 25°C of 100 mPa•s was obtained.

[0097] The liquid was confirmed, by an analysis using nuclear magnetic resonance spectroscopy, to be an organopolysiloxane represented by the following average unit formula:

$(EpMeSiO_{2/2})_{0.51}(PhSiO_{3/2})_{0.49}(MeO_{1/2})_{0.21}$.

The epoxy equivalent weight of the organopolysiloxane was 310 g/mol. The methoxy group content of the organopolysiloxane was 4.1 % by weight. The weight average molecular weight (Mw) was 1,400. The dispersity (Mw/Mn) was 1.28. The refractive index was 1.491.

[0098]

[Practical Example 1]

1.02 g of the organopolysiloxane prepared in Reference Example 1, which is represented by the following average unit formula:

$(EpMeSiO_{2/2})_{0.24}(NaphSiO_{3/2})_{0.76}(MeO_{1/2})_{0.05}$,

0.98 g of an epoxy compound (3',4'-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate; Celloxide 2021P, manufactured by Daicel Chemical Industries Ltd.), 1.58 g of an acid anhydride curing agent (3- or 4-methyl-hexahydrophthalic anhydride; HN 5500E, manufactured by Hitachi Chemical Co., Ltd.), and 0.0236 g of a curing accelerator (methyltributylphosphonium dimethylphosphate; Hishicolin PX-4MP, manufactured by Nippon Chemical Industrial Co., Ltd.) were mixed to prepare a liquid curable silicone composition.

[0099] This curable silicone composition was coated on a quartz glass plate and cured by being heated for one hour at 150°C. The obtained cured product was clear and colorless, and had a storage elastic modulus at 25°C of 1.84 MPa. In addition, this cured product had a refractive index of 1.5284 at a wavelength of 632.8 nm.

[0100]

[Practical Example 2]

2.04 g of the organopolysiloxane prepared in Reference Example 2, which is represented by the following average unit formula:

$(EpMeSiO_{2/2})_{0.50}(NaphSiO_{3/2})_{0.50}$,

0.95 g of an acid anhydride curing agent (3- or 4-methyl-hexahydrophthalic anhydride; HN 5500E, manufactured by Hitachi Chemical Co., Ltd.), 0.0300 g of a curing accelerator (methyltributylphosphonium dimethylphosphate; Hishicolin PX-4MP, manufactured by Nippon Chemical Industrial Co., Ltd.), and further toluene were mixed to prepare a toluene solution of a curable silicone composition (concentration: about 30 % by weight).

[0101] This curable silicone composition was coated on a quartz glass plate. After the toluene was volatilized by air-drying for one day, the curable silicone composition was cured by being heated for one hour at 150°C. The obtained cured product was clear and colorless, and had a storage elastic modulus at 25°C of 30.3 MPa. In addition, this cured product had a refractive index of 1.5524 at a wavelength of 632.8 nm.

[0102]

[Practical Example 3]

1.99 g of the organopolysiloxane prepared in Reference Example 3, which is represented by the following average unit formula:

$(EpMeSiO_{2/2})_{0.49}(NaphSiO_{3/2})_{0.51}(MeO_{1/2})_{0.05}$,

0.94 g of an acid anhydride curing agent (3- or 4-methyl-hexahydrophthalic anhydride; HN 5500E, manufactured by Hitachi Chemical Co., Ltd.), 0.0195 g of a curing accelerator (methyltributylphosphonium dimethylphosphate; Hishicolin PX-4MP, manufactured by Nippon Chemical Industrial Co., Ltd.), and further toluene were mixed to prepare a toluene solution of a curable silicone composition (concentration: about 30 % by weight).

[0103] This curable silicone composition was coated on a quartz glass plate. After the toluene was volatilized by air-drying for one day, the curable silicone composition was cured by being heated for one hour at 150°C. The obtained cured product was clear and colorless, and had a storage elastic modulus at 25°C of 12.9 MPa. In addition, this cured product had a refractive index of 1.5484 at a wavelength of 632.8 nm.

[0104]

[Comparative Example 1]

2.01 g of the organopolysiloxane prepared in Reference Example 4, which is represented by the following average unit formula:

$(EpSiO_{3/2})_{0.24}(NaphSiO_{3/2})_{0.76}$,

0.49 g of an acid anhydride curing agent (3- or 4-methyl-hexahydrophthalic anhydride; HN 5500E, manufactured by Hitachi Chemical Co., Ltd.), 0.0236 g of a curing accelerator (methyltributylphosphonium dimethylphosphate; Hishicolin PX-4MP, manufactured by Nippon Chemical Industrial Co., Ltd.), and further toluene were mixed to prepare a toluene solution of a curable silicone composition (concentration: about 30 % by weight).

[0105] This curable silicone composition was coated on a quartz glass plate. After the toluene was volatilized by air-drying for one day, the curable silicone composition was cured by being heated for one hour at 150°C. The obtained cured product was clear and colorless, and had a storage elastic modulus at 25°C of 68.7 MPa. In addition, this cured product had a refractive index of 1.6029 at a wavelength of 632.8 nm.

[0106]

[Comparative Example 2]

1.02 g of the organopolysiloxane prepared in Reference Example 4, which is represented by the following average unit formula:

$(EpSiO_{3/2})_{0.24}(NaphSiO_{3/2})_{0.76}$,

0.99 g of an epoxy compound (3',4'-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate; Celloxide 2021P, manufactured by Daicel Chemical Industries Ltd.), 1.57 g of an acid anhydride curing agent (3- or 4-methyl-hexahydrophthalic anhydride; HN 5500E, manufactured by Hitachi Chemical Co., Ltd.), and 0.0236 g of a curing accelerator (methyltributylphosphonium dimethylphosphate; Hishicolin PX-4MP, manufactured by Nippon Chemical Industrial Co., Ltd.) were mixed to prepare a liquid curable silicone composition.

[0107] This curable silicone composition was coated on a quartz glass plate and cured by being heated for one hour at 150°C. The obtained cured product was clear and colorless, and had a storage elastic modulus at 25°C of 1.46 MPa. In addition, this cured product had a refractive index of 1.5379 at a wavelength of 632.8 nm.

[0108]

[Comparative Example 3]

2.07 g of the organopolysiloxane prepared in Reference Example 5, which is represented by the following average unit formula:

$(NaphMeSiO_{2/2})_{0.49}(EpSiO_{3/2})_{0.51}$,

0.95 g of an acid anhydride curing agent (3- or 4-methyl-hexahydrophthalic anhydride; HN 5500E, manufactured by Hitachi Chemical Co., Ltd.), 0.0214 g of a curing accelerator (methyltributylphosphonium dimethylphosphate; Hishicolin PX-4MP, manufactured by Nippon Chemical Industrial Co., Ltd.), 0.0158 g of a 10.8 % by weight toluene solution of pentaerythritol tetrakis [3-(3,5-di-tert-butyl-hydroxyphenyl)propionate] as an antioxidant, and further toluene were mixed to prepare a toluene solution of a curable silicone composition (concentration: about 30 % by weight).

[0109] This curable silicone composition was coated on a quartz glass plate. After the toluene was volatilized by air-drying for one day, the curable silicone composition was cured by being heated for one hour at 150°C. The obtained cured product was clear and colorless, and had a storage elastic modulus at 25°C of 0.89 MPa. In addition, this cured product had a refractive index of 1.5481 at a wavelength of 632.8 nm.

[0110]

[Comparative Example 4]

2.05 g of the organopolysiloxane prepared in Reference Example 6, which is represented by the following average unit formula:

$(NaphMeSiO_{2/2})_{0.45}(Me_2SiO_{2/2})_{0.10}(EpSiO_{3/2})_{0.45}(MeO_{1/2})_{0.01}$,

0.95 g of an acid anhydride curing agent (3- or 4-methyl-hexahydrophthalic anhydride; HN 5500E, manufactured by Hitachi Chemical Co., Ltd.), 0.0205 g of a curing accelerator (methyltributylphosphonium dimethylphosphate; Hishicolin PX-4MP, manufactured by Nippon Chemical Industrial Co., Ltd.), and further toluene were mixed to prepare a toluene solution of a curable silicone composition (concentration: about 30 % by weight).

[0111] This curable silicone composition was coated on a quartz glass plate. After the toluene was volatilized by air-drying for one day, the curable silicone composition was cured by being heated for one hour at 150°C. The obtained cured product was clear and colorless, and had a storage elastic modulus at 25°C of 0.11 MPa. In addition, this cured product had a refractive index of 1.5499 at a wavelength of 632.8 nm.

[0112]

[Comparative Example 5]

1.07 g of the organopolysiloxane prepared in Reference Example 7, which is represented by the following average unit formula:

$(EpMeSiO_{2/2})_{0.51}(PhSiO_{3/2})_{0.49}$,

0.97 g of an epoxy compound (3',4'-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate; Celloxide 2021P, manufactured by Daicel Chemical Industries Ltd.), 1.86 g of an acid anhydride curing agent (3- or 4-methyl-hexahydrophthalic anhydride; HN 5500E, manufactured by Hitachi Chemical Co., Ltd.), and 0.0208 g of a curing accelerator (methyltributylphosphonium dimethylphosphate; Hishicolin PX-4MP, manufactured by Nippon Chemical Industrial Co., Ltd.) were mixed to prepare a curable silicone composition.

[0113] This curable silicone composition was coated on a quartz glass plate and cured by being heated for one hour at 150°C. The obtained cured product was clear and colorless, and had a storage elastic modulus at 25°C of 8.0 MPa. In addition, this cured product had a refractive index of 1.5073 at a wavelength of 632.8 nm.

[0114]

[Comparative Example 6]

2.00 g of the organopolysiloxane prepared in Reference Example 8, which is represented by the following average unit formula:

$(EpMeSiO_{2/2})_{0.51}(PhSiO_{3/2})_{0.49}(MeO_{1/2})_{0.21}$,

1.07 g of an acid anhydride curing agent (3- or 4-methyl-hexahydrophthalic anhydride; HN 5500E, manufactured by Hitachi Chemical Co., Ltd.), and 0.0154 g of a curing accelerator (methyltributylphosphonium dimethylphosphate; Hishicolin PX-4MP, manufactured by Nippon Chemical Industrial Co., Ltd.) were mixed to prepare a curable silicone composition.

[0115] This curable silicone composition was coated on a quartz glass plate and cured by being heated for one hour at 150°C. The obtained cured product was clear and colorless, and had a storage elastic modulus at 25°C of 11.8 MPa. In addition, this cured product had a refractive index of 1.5098 at a wavelength of 632.8 nm.

Industrial Applicability

[0116] The curable silicone composition of the present invention is cured to form a cured product with a high refractive index, high transparency, and excellent heat resistance and flexibility, and especially a cured product having a low water vapor permeability. Therefore, the curable silicone composition can be used as an adhesive, a potting agent, a protective coating agent, or an underfill agent for electrical/electronic use. In particular, since the optical transmittance is high, the curable silicone composition is suitable as a sealing agent or a covering agent for an LED element or as a lens forming material.

Description of Symbols

[0117]

1	Polyphthalamide (PPA) resin case
2	LED chip
3	Inner lead
4	Bonding wire
5	Cured product of the curable silicone composition

CLAIMS

1. A curable silicone composition comprising:

(A) an organopolysiloxane represented by the following average unit formula:

$$(R^1R^2SiO_{2/2})_a(R^3SiO_{3/2})_b(XO_{1/2})_c$$

wherein R^1 is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, or a phenyl group; R^2 is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, a phenyl group, or an epoxy group-containing organic group, provided that at least one R^2 in a molecule is the epoxy group-containing organic group; R^3 is a condensed polycyclic aromatic group or a condensed polycyclic aromatic group-containing organic group; X is an alkyl group having from 1 to 3 carbon atoms or a hydrogen atom; **a** is a number from 0.20 to 0.60, **b** is a number from 0.40 to 0.80, a sum of **a** and **b** is 1.00, and **c** is a number from 0 to 0.5;

(B) a curing agent; and

(C) a curing accelerator.

2. The curable silicone composition according to claim 1, wherein, in component (A), the epoxy group-containing organic group for R^2 is a glycidoxyalkyl group, an epoxycycloalkylalkyl group, or an oxiranylalkyl group.

3. The curable silicone composition according to claim 1, wherein, in component (A), R^3 is a naphthyl group or a naphthyl ethyl group.

4. The curable silicone composition according to claim 1, wherein component (A) contains at least 10 mol% of epoxy group-containing organic groups relative to all of R^1 and R^2 in a molecule.

5. The curable silicone composition according to claim 1, wherein component (B) is an acid anhydride-based curing agent.

6. The curable silicone composition according to claim 1, wherein a content of component (B) is from 1 to 200 parts by weight per 100 parts by weight of component (A).

7. The curable silicone composition according to claim 1, wherein a content of component (C) is from 0.01 to 5 parts by weight per 100 parts by weight of component (A).

8. A cured product produced by curing the curable silicone composition described in any one of claims 1 to 7.

9. The cured product according to claim 8, wherein a refractive index of the cured product at 25°C at a wavelength of 632.8 nm is greater than or equal to 1.5.

10. An optical semiconductor device formed by covering or sealing an optical semiconductor element with the curable silicone composition described in any one of claims 1 to 7.

FIG. 1

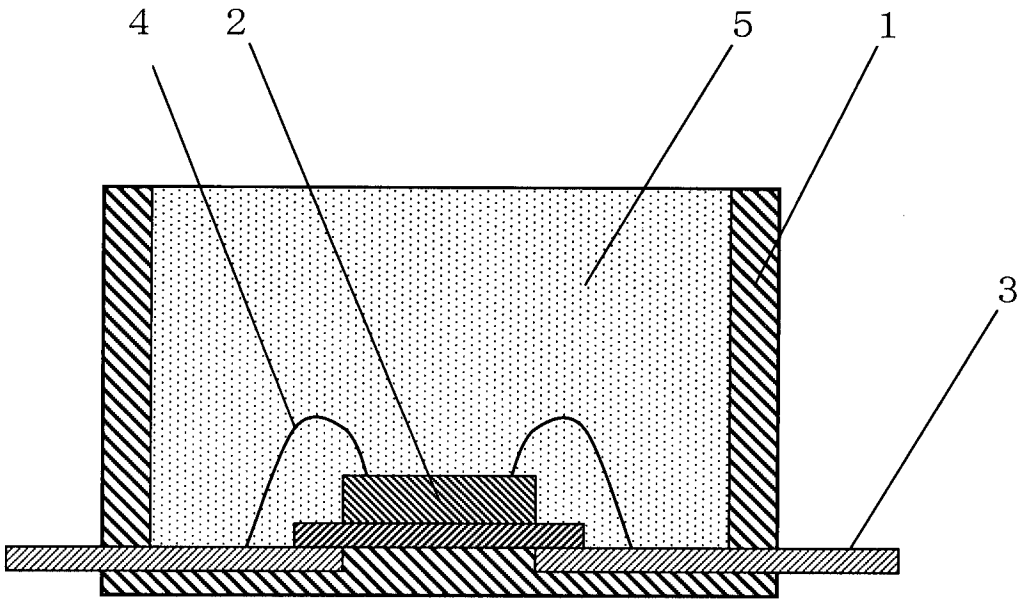
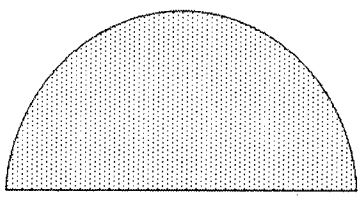


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2014/055529

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G77/14 C08L83/06 H01L23/29
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G C08L H01L

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/160410 A1 (SAGAWA TAKASHI [JP] ET AL) 30 June 2011 (2011-06-30)	1-4,6-10
Y	practical example 2; paragraphs [0019] - [0024] paragraphs [0012], [0029], [0079]	1-10
Y	US 2012/178022 A1 (KAMOGAWA MASAO [JP] ET AL) 12 July 2012 (2012-07-12) paragraphs [0023], [0071]	1-4,6-10
Y	PHAM ET AL: "Epoxy Resins", 1 January 2004 (2004-01-01), ENCYCLOPEDIA OF POLYMER SCIENCE AND TECHNOLOGY,, PAGE(S) 1 - 127, XP007920796, pages 735-738; tables 13-14	5

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 April 2014	17/04/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Dalet, Pierre

2

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2014/055529

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2012/173460 A2 (LG CHEM LTD) 20 December 2012 (2012-12-20) abstract	5
Y	US 2009/214870 A1 (MORITA YOSHITSUGU [JP] ET AL) 27 August 2009 (2009-08-27) application example 1	5
Y	WO 2012/091000 A1 (DOW CORNING TORAY CO LTD [JP]; MASATOMI TORU [JP]; YOSHIZAWA TAKESHI [) 5 July 2012 (2012-07-05) abstract	5
Y,P	-& EP 2 660 263 A1 (DOW CORNING TORAY CO LTD [JP]) 6 November 2013 (2013-11-06) practical example F1; paragraph [0035]; claim 18	5

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/JP2014/055529

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011160410 A1	30-06-2011	CN 102066493 A	18-05-2011
		EP 2326686 A1	01-06-2011
		JP 2010001335 A	07-01-2010
		KR 20110018916 A	24-02-2011
		RU 2010151565 A	27-07-2012
		TW 201000561 A	01-01-2010
		US 2011160410 A1	30-06-2011
		WO 2009154260 A1	23-12-2009
US 2012178022 A1	12-07-2012	CN 102472964 A	23-05-2012
		EP 2485091 A1	08-08-2012
		JP 5423802 B2	19-02-2014
		KR 20120074272 A	05-07-2012
		TW 201120144 A	16-06-2011
		US 2012178022 A1	12-07-2012
		WO 2011040248 A1	07-04-2011
WO 2012173460 A2	20-12-2012	CN 103608408 A	26-02-2014
		EP 2722366 A2	23-04-2014
		KR 20120139614 A	27-12-2012
		WO 2012173460 A2	20-12-2012
US 2009214870 A1	27-08-2009	AT 408649 T	15-10-2008
		CN 101142280 A	12-03-2008
		EP 1858983 A1	28-11-2007
		JP 5166677 B2	21-03-2013
		JP 2006257115 A	28-09-2006
		KR 20070117597 A	12-12-2007
		TW I383025 B	21-01-2013
		US 2009214870 A1	27-08-2009
		WO 2006098493 A1	21-09-2006
WO 2012091000 A1	05-07-2012	CN 103370352 A	23-10-2013
		EP 2660263 A1	06-11-2013
		KR 20130133812 A	09-12-2013
		TW 201237094 A	16-09-2012
		US 2013338265 A1	19-12-2013
		WO 2012091000 A1	05-07-2012
EP 2660263 A1	06-11-2013	CN 103370352 A	23-10-2013
		EP 2660263 A1	06-11-2013
		KR 20130133812 A	09-12-2013
		TW 201237094 A	16-09-2012
		US 2013338265 A1	19-12-2013
		WO 2012091000 A1	05-07-2012