



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

WIPO | PCT

(10) International Publication Number
WO 2014/136806 A1

(51) International Patent Classification:

C08G 77/14 (2006.01) *C08G 77/00* (2006.01)
C08L 83/06 (2006.01)

(21) International Application Number:

PCT/JP2014/055531

(22) International Filing Date:

26 February 2014 (26.02.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2013-043000 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, Chigusaigaigan, Ichihara-shi, Chiba,
2990108 (JP). **ONODERA, Satoshi**; c/o Dow Corning
Toray Co., Ltd., 2-2, Chigusaigaigan, 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: ORGANOPOLYSILOXANE AND MANUFACTURING METHOD THEREOF

(57) Abstract: The present invention relates to an organopolysiloxane represented by the average unit formula: $(R^1R^2SiO_{2/2})_a(R^3-SiO_{3/2})_b(XO_{1/2})_c$, 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. The organopolysiloxane has a high refractive index, and is monodispersed and curable to form a cured product having an adequate elastic modulus.



WO 2014/136806 A1

DESCRIPTION

ORGANOPOLYSILOXANE AND MANUFACTURING METHOD THEREOF

Technical Field

[0001] The present invention relates to an organopolysiloxane containing epoxy group-containing organic groups, and condensed polycyclic aromatic groups or condensed polycyclic aromatic group-containing organic groups, and a manufacturing method thereof.

[0002] Priority is claimed on Japanese Patent Application No. 2013-043000, filed on March 5, 2013, the content of which is incorporated herein by reference.

Background Art

[0003] Organopolysiloxanes comprising 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) are used as optical materials, such as sealing agents for LEDs and lens-molding materials, due to their excellent heat resistance, light resistance, and transparency. In these applications, organopolysiloxanes having high refractive indices are particularly preferred. To increase the refractive index of an organopolysiloxane, 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-naphthylmethyl dimethoxysilane, 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.

- 5 [0006] Additionally, 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.

10 Prior Art Documents

Patent Documents

[0007]

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

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

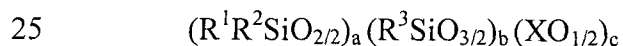
Summary of Invention

Technical Problem

- 20 [0008] An object of the present invention is to provide an organopolysiloxane that has a high refractive index, and is monodispersed and curable to form a cured product having an adequate elastic modulus, and also to provide a manufacturing method thereof.

Solution to Problem

[0009] The organopolysiloxane of the present invention is represented by the following average unit formula:



- 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
- 30

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.

[0010] In the formula, 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, at least 10 mol% of all of R^1 and R^2 in a molecule are preferably epoxy group-containing organic groups.

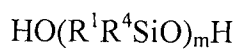
[0011] The manufacturing method of the present invention is a manufacturing method of the organopolysiloxane described above. The manufacturing method comprises a step of, in the presence of an acid or an alkali, hydrolyzing and condensation reacting:

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



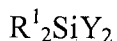
wherein R^1 is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, or a phenyl group; R^4 is an epoxy group-containing organic group; and Y is a hydrolysable group; and/or

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



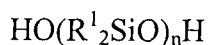
wherein R^1 and R^4 are synonymous with those described above, and **m** is an integer from 1 to 100; and

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



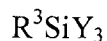
wherein R^1 and Y are synonymous with those described above; and/or

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



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):



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.

[0012] In the silane compound represented by the general formula (I) and the siloxane compound represented by the general formula (II), R^4 is preferably a glycidoxyalkyl group, an epoxycyclohexyl alkyl group, or an oxiranylalkyl group. In the silane compound

represented by the general formula (V), R^3 is preferably a naphthyl group or a naphthyl ethyl group.

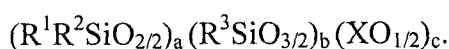
Effects of Invention

[0013] The organopolysiloxane of the present invention is characterized by having a high refractive index, and being monodispersed and curable to form a cured product having an adequate elastic modulus. In addition, the manufacturing method of the present invention is characterized by being able to efficiently manufacture such an organopolysiloxane.

Detailed Description of the Invention

[0014] First, the organopolysiloxane of the present invention will be described in detail.

[0015] The organopolysiloxane of the present invention is represented by the following average unit formula:



[0016] 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.

[0017] 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, and preferably at least two, R^2 are epoxy group-containing organic groups. In particular, because the curability of the organopolysiloxane of the present invention is good, 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%.

[0018] 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 curable silicone composition containing the organopolysiloxane as a main component can be lowered.

[0019] 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.

[0020] 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 of the organopolysiloxane 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 organopolysiloxane will exhibit a high refractive index and become monodispersed.

[0021] In the formula, **c** indicates a proportion of a unit represented by the formula: $\text{XO}_{1/2}$ that is formed in the course of manufacturing the organopolysiloxane of the present invention, 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 the organopolysiloxane itself will be enhanced. The above units are preferably contained in the organopolysiloxane because the adhesive properties of a curable silicone composition containing, as a main component, the organopolysiloxane of the present invention can be enhanced, and/or the bonding properties toward substrates of the cured product of the curable silicone composition can be enhanced.

[0022] The molecular weight of this type of organopolysiloxane of the present invention is not particularly limited, but from the perspectives of excellent handling/workability and the like, 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 such an organopolysiloxane of the present invention at 25°C is not particularly limited, and examples of the form include oil-like, paste-like, resin-like, gum-like, and solid (powder).

[0023] Furthermore, the refractive index at 25°C and at a wavelength of 632.8 nm of the organopolysiloxane of the present invention is preferably greater than or equal to 1.50, and particularly preferably greater than or equal to 1.53.

[0024] Since the organopolysiloxane of the present invention contains an epoxy group-containing organic group in the molecule, a curable silicone composition can be formed by compounding a curing agent and a curing accelerator in the organopolysiloxane of the present invention.

[0025] The curing agent is not particularly limited as long as the curing agent reacts with an epoxy group in the organopolysiloxane of the present invention to cure.

Examples of the curing agent 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, phenolnovolac, cresolnovolac, 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 carbon atoms (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); and aromatic acid anhydrides such as phthalic anhydride, trimellitic anhydride, and pyromellitic anhydride.

[0026] Although the compounded amount of the curing agent is not particularly limited, the compounded amount is preferably in a range of 1 to 200 parts by weight, and particularly preferably in a range of 20 to 160 parts by weight, per 100 parts by weight of the organopolysiloxane of the present invention because the organopolysiloxane of the present invention can be sufficiently cured and the resulting cured product exhibits good heat resistance and weather resistance.

[0027] The curing accelerator is not particularly limited as long as the curing accelerator accelerates the curing reaction between the curing agent and the organopolysiloxane of the present invention. Examples of the curing accelerators 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.

[0028] Although the compounded amount of the curing accelerator is not particularly limited, the compounded amount is preferably in a range of 0.01 to 5 parts by weight, and particularly preferably in a range of 0.1 to 5 parts by weight, per 100 parts by weight of the organopolysiloxane of the present invention because the curing of the organopolysiloxane of the present invention can be sufficiently accelerated and the resulting cured product exhibits good heat resistance and weather resistance.

[0029] Furthermore, from the perspectives 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 curable silicone composition containing as a main component the organopolysiloxane of the present invention. Although the compounded amount of the epoxy compound is not particularly limited, the compounded amount is preferably not greater than 200 parts by weight, and particularly preferably not greater than 100 parts by weight, per 100 parts by weight of the organopolysiloxane of the present invention.

[0030] The organopolysiloxane of the present invention can be cured to form a cured product that 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.

[0031] The manufacturing method of the organopolysiloxane of the present invention will now be described in detail.

[0032] The silane compound represented by the following general formula (I):



is a raw material for introducing a D unit having an epoxy group-containing organic group to the resulting organopolysiloxane.

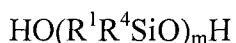
[0033] In the formula, R^1 is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group having from 2 to 12 carbon atoms, or a phenyl group, and examples thereof are synonymous with the groups described above. Of these, a methyl group is preferable.

[0034] In the formula, examples of the epoxy group-containing organic group for R⁴ 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.

[0035] 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.

[0036] Examples of such a silane compound include 3-glycidoxypropyl methyldimethoxysilane, 3-glycidoxypropyl methyldiethoxysilane, 3-glycidoxypropyl ethyldimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyl methyldimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyl methyldiethoxysilane, 4-oxiranylbutyl methyldimethoxysilane, 8-oxiranyloctyl methyldimethoxysilane, 3-glycidoxypropyl methyldiacetoxysilane, 3-glycidoxypropyl ethyldiacetoxysilane, 2-(3,4-epoxycyclohexyl)ethyl methyldiacetoxysilane, 3-glycidoxypropyl methyldichlorosilane, 3-glycidoxypropyl ethyldichlorosilane, and 2-(3,4-epoxycyclohexyl)ethyl methyldichlorosilane.

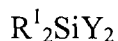
[0037] The siloxane compound represented by the following general formula (II):



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

[0038] In the formula, R¹ 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, R⁴ 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.

[0039] The silane compound represented by the following general formula (III):

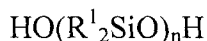


is an optional raw material for introducing a D unit that is free of an epoxy group-containing organic group to the resulting organopolysiloxane.

5 [0040] 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.

10 [0041] Examples of such a silane compound include dimethyldimethoxysilane, dimethyldiethoxysilane, methylphenyldimethoxysilane, methylphenyldiethoxysilane, methylethyldimethoxysilane, ethylphenyldimethoxysilane, diphenyldimethoxysilane, diphenyldiethoxysilane, dimethyldiacetoxysilane, methylphenyldiacetoxysilane, ethylphenyldiacetoxysilane, diphenyldiacetoxysilane, dimethyldichlorosilane,
15 methylphenyldichlorosilane, and diphenyldichlorosilane.

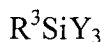
[0042] The siloxane compound represented by the following general formula (IV):



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

20 [0043] 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.

25 [0044] The silane compound represented by the following general formula (V):



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 resulting organopolysiloxane.

30 [0045] 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.

[0046] Examples of such a silane compound include naphthyl trimethoxysilane, 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.

[0047] The manufacturing method of the present invention 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).

[0048] In the manufacturing method of the present invention, the compounding amount of each of the raw materials is such that the proportion of the D unit introduced to the resulting organopolysiloxane (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 (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.

[0049] 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 D unit, is not particularly limited. However, from the perspective of the curability of the resulting organopolysiloxane 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%.

[0050] Examples of the acid that can be used in the manufacturing method of the present invention 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 of the present invention include inorganic alkalis such as potassium hydroxide, sodium hydroxide, and cesium hydroxide; and organic base compounds such as triethylamine, diethylamine, monoethanolamine, diethanolamine, triethanolamine, ammonia water, tetramethylammonium hydroxide, alkoxysilanes having an amino group, and aminopropyltrimethoxysilane.

[0051] In the manufacturing method of the present invention, 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.

[0052] In order to accelerate the hydrolysis and condensation reaction of each of the components in the manufacturing method of the present invention, 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.

Examples

[0053] The organopolysiloxane and the manufacturing method thereof of the present invention will now be described in greater detail 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.

[0054]

[Weight average molecular weight and dispersity]

The weight average molecular weight (M_w) and number average molecular weight (M_n) in terms of standard polystyrene of the organopolysiloxane were determined by gel

permeation chromatography using an RI detector. The dispersity (M_w/M_n) was determined from these values.

[0055]

[Refractive index]

5 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.

[0056]

[Viscosity]

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

[0057]

[Epoxy equivalent weight]

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

[0058]

[Methoxy group content]

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

[0059] Additionally, the characteristics of the curable silicone composition containing the organopolysiloxane as a main component, and a curing agent and a curing accelerator compounded thereto, and the characteristics of the cured product thereof were evaluated as follows.

25 [0060]

[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.

30 [0061]

[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.

[0062]

[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.

[0063]

[Transparency of the cured product]

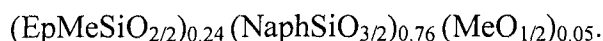
The transparency of the cured product prepared by the method described above was confirmed visually.

[0064]

[Practical Example 1]

49.67 g of 1-naphthyltrimethoxysilane, 14.69 g of 3-glycidoxypromethylmethoxydimethoxysilane, 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 were 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.

[0065] The solid was confirmed, by an analysis using nuclear magnetic resonance spectroscopy, to be an organopolysiloxane represented by the following average unit formula:



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.

[0066]

[Practical Example 2]

5 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.
10 After the addition was completed, the mixture was refluxed for one hour. Produced methanol and excess water were 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
15 by distillation. Thus, 53.70 g of transparent brown gum-like substance (at room temperature) was obtained.

[0067] The substance was confirmed, by an analysis using nuclear magnetic resonance spectroscopy, to be an organopolysiloxane represented by the following average unit formula:

20 $(\text{EpMeSiO}_{2/2})_{0.50} (\text{NaphSiO}_{3/2})_{0.50}$.

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.

[0068]

[Practical 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
30 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 were 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 of 1,600 mPa•s was obtained.

[0069] The liquid was confirmed, by an analysis using nuclear magnetic resonance spectroscopy, to be an organopolysiloxane represented by the following average unit formula:



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.

[0070]

[Practical Example 4]

49.67 g of 1-naphthyltrimethoxysilane, 14.69 g of 3-glycidoxypopyl 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 0.10 g of cesium hydroxide monohydrate, 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 were 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, 48.77 g of transparent pale yellow liquid (at room temperature) was obtained.

[0071] The liquid was confirmed, by an analysis using nuclear magnetic resonance spectroscopy, to be an organopolysiloxane represented by the following average unit formula:



The epoxy equivalent weight of the organopolysiloxane was 740 g/mol. The methoxy group content of the organopolysiloxane was 0.1 % by weight. The weight average

molecular weight (Mw) was 1,300. The dispersity (Mw/Mn) was 1.07. The refractive index was 1.600.

[0072]

[Practical Example 5]

5 37.25 g of 1-naphthyltrimethoxysilane, 33.05 g of 3-glycidoxypentyl
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 0.12 g of cesium hydroxide monohydrate, 4.73 g of water, and 4.73 g of
methanol was gradually added to the reaction vessel using the dropping funnel. After the
10 addition was completed, the mixture was refluxed for one hour. Produced methanol and
excess water were 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.
15 Thus, 58.63 g of transparent yellow liquid with a viscosity of 800 mPa•s was obtained.

[0073] The liquid was confirmed, by an analysis using nuclear magnetic resonance spectroscopy, to be an organopolysiloxane represented by the following average unit formula:



20 The epoxy equivalent weight of the organopolysiloxane was 360 g/mol. The methoxy group content of the organopolysiloxane was 3.9 % by weight. The weight average molecular weight (Mw) was 1,200. The dispersity (Mw/Mn) was 1.27. The refractive index was 1.539.

[0074]

25 [Practical Example 6]

77.48 g of 1-naphthyltrimethoxysilane, 7.05 g of 3-glycidoxypentyl
methyldimethoxysilane, and 4.16 g of dimethylpolysiloxane represented by the following
formula:



30 and 56.69 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 0.11 g of cesium hydroxide monohydrate, 13.50 g of water, and 13.50 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 were 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, 66.53 g of slightly yellow solid (at room temperature) was obtained.

[0075] The solid was confirmed, by an analysis using nuclear magnetic resonance spectroscopy, to be an organopolysiloxane represented by the following average unit formula:



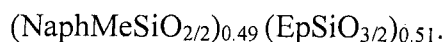
The epoxy equivalent weight of the organopolysiloxane was 2,100 g/mol. Almost no methoxy group was observed, and the methoxy group content was less than 0.1 % by weight. The weight average molecular weight (Mw) was 1,300. The dispersity (Mw/Mn) was 1.13. The refractive index was 1.614.

[0076]

[Comparative Example 1]

50.00 g of 1-naphthyl methyldimethoxysilane, 50.85 g of 3-glycidoxypopyl 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 were 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.

[0077] The solid was confirmed, by an analysis using nuclear magnetic resonance spectroscopy, to be an organopolysiloxane represented by the following average unit formula:



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.

5 [0078]

[Comparative Example 2]

50.00 g of 1-naphthyl methyldimethoxysilane, 50.85 g of 3-glycidoxypopyl trimethoxysilane, and 3.54 g of dimethylpolysiloxane represented by the following formula:

10 $\text{HO}(\text{Me}_2\text{SiO})_{10}\text{H}$,

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 were 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.

[0079] The solid was confirmed, by an analysis using nuclear magnetic resonance spectroscopy, to be an organopolysiloxane represented by the following average unit formula:



25 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.

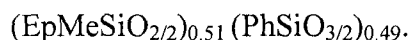
[0080]

30 [Comparative Example 3]

59.40 g of phenyltrimethoxysilane, 66.10 g of 3-glycidoxypopyl 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 were 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 of 13,400 mPa•s was obtained.

[0081] The liquid was confirmed, by an analysis using nuclear magnetic resonance spectroscopy, to be an organopolysiloxane represented by the following average unit formula:



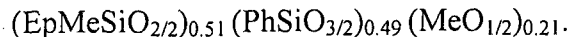
The epoxy equivalent weight of the organopolysiloxane was 300 g/mol. Almost no methoxy group was observed, and the methoxy group content was less than 0.1 % by weight. The weight average molecular weight (Mw) was 2,600. The dispersity (Mw/Mn) was 1.34. The refractive index was 1.513.

[0082]

[Comparative Example 4]

59.40 g of phenyltrimethoxysilane, 66.10 g of 3-glycidoxypopyl 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 were 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 of 100 mPa•s was obtained.

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



- 5 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.

[0084]

- 10 [Comparative Example 5]

49.67 g of 1-naphthyltrimethoxysilane, 15.76 g of 3-glycidoxypentyl 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
15 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 were 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-
20 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.

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

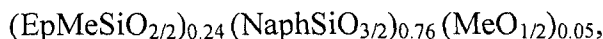
- 25 $(\text{EpSiO}_{3/2})_{0.24} (\text{NaphSiO}_{3/2})_{0.76}.$

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.

- 30 [0086]

[Applied Example 1]

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



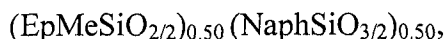
0.98 g of an epoxy compound (3',4'-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate; Celloxide 2021P, manufactured by Daicel Chemical Industries Ltd.), 1.58 g of an acid anhydride-based curing agent (3- or 4-methyl-hexahydrophthalic anhydride; HN 5500E, manufactured by Hitachi Chemical Co., Ltd.), 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.

[0087] 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 of 1.84 MPa and a refractive index of 1.5284.

[0088]

[Applied Example 2]

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



0.95 g of an acid anhydride-based 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).

[0089] 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 of 30.3 MPa and a refractive index of 1.5524.

[0090]

[Applied Example 3]

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



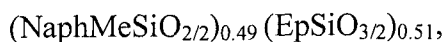
0.94 g of an acid anhydride-based curing agent (3- or 4-methyl-hexahydrophthalic anhydride; HN 5500E, manufactured by Hitachi Chemical Co., Ltd.), 0.0195 g of a curing accelerator (methyltributylphosphonium dimethylphosphate; Hishicolin PX-4MP, manufactured by Nippon Chemical Industrial Co., Ltd.), and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

[0091] 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 of 12.9 MPa and a refractive index of 1.5484.

[0092]

[Comparative Applied Example 1]

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



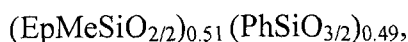
0.95 g of an acid anhydride-based curing agent (3- or 4-methyl-hexahydrophthalic anhydride; HN 5500E, manufactured by Hitachi Chemical Co., Ltd.), 0.0214 g of a curing accelerator (methyltributylphosphonium dimethylphosphate; Hishicolin PX-4MP, manufactured by Nippon Chemical Industrial Co., Ltd.), 0.0158 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).

[0093] 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 of 0.89 MPa and a refractive index of 1.5481.

[0094]

[Comparative Applied Example 2]

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



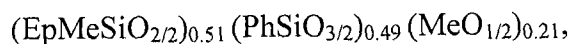
0.97 g of an epoxy compound (3',4'-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate; Celloxide 2021P, manufactured by Daicel Chemical Industries Ltd.), 1.86 g of an acid anhydride-based curing agent (3- or 4-methyl-hexahydrophthalic anhydride; HN 5500E, manufactured by Hitachi Chemical Co., Ltd.), 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.

[0095] 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 of 8.0 MPa and a refractive index of 1.5073.

[0096]

[Comparative Applied Example 3]

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



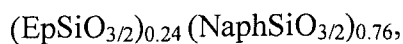
1.07 g of an acid anhydride-based curing agent (3- or 4-methyl-hexahydrophthalic anhydride; HN 5500E, manufactured by Hitachi Chemical Co., Ltd.), and 0.0154 g of a curing accelerator (methyltributylphosphonium dimethylphosphate; Hishicolin PX-4MP, manufactured by Nippon Chemical Industrial Co., Ltd.)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

[0097] 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 of 11.8 MPa and a refractive index of 1.5098.

[0098]

[Comparative Applied Example 4]

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



0.49 g of an acid anhydride-based 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).

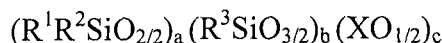
[0099] This curable silicone composition was coated on a quartz glass plate. After the toluene was volatilized by air-drying for one day, the curable silicone composition was cured by being heated for one hour at 150°C. The obtained cured product was clear and colorless, and had a storage elastic modulus of 68.7 MPa and a refractive index of 1.6029.

Industrial Applicability

[0100] Since the organopolysiloxane of the present invention is curable via the reaction of the epoxy group, and forms a cured product that is transparent and has a high refractive index and an adequate elastic modulus, the organopolysiloxane of the present invention is preferably used in optical materials such as resists, coatings, films, sheets, adhesives, coating materials, sealing materials, lenses, light guide plates, and optical waveguides, and particularly preferably used in sealing materials, coating agents, or adhesives for LED elements; coatings for electrodes or the like around an element; or lens forming materials.

CLAIMS

1. An organopolysiloxane represented by the following average unit formula:



wherein R^1 is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group
 5 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
 10 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.

2. The organopolysiloxane according to claim 1, wherein the epoxy group-
 containing organic group for R^2 is a glycidoxyalkyl group, an epoxycycloalkylalkyl
 15 group, or an oxiranylalkyl group.

3. The organopolysiloxane according to claim 1, wherein R^3 is a naphthyl group
 or a naphthyl ethyl group.

4. The organopolysiloxane according to claim 1, wherein at least 10 mol% of all
 of R^1 and R^2 in a molecule are epoxy group-containing organic groups.

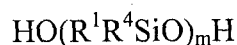
5. A manufacturing method of the organopolysiloxane described in claim 1, the
 manufacturing method comprising a step of, in the presence of an acid or an alkali,
 hydrolyzing and condensation reacting:

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



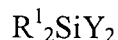
wherein R^1 is an alkyl group having from 1 to 12 carbon atoms, an alkenyl group
 25 having from 2 to 12 carbon atoms, or a phenyl group; R^4 is an epoxy group-containing
 organic group; and Y is a hydrolysable group; and/or

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

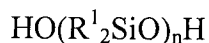


wherein R^1 and R^4 are synonymous with those described above, and m is an integer from 1 to 100; and

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

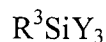


- 5 wherein R^1 and Y are synonymous with those described above; and/or
a siloxane compound represented by the following general formula (IV):



wherein R^1 is synonymous with those described above, and n is an integer from 1 to 100;

- 10 with a silane compound represented by the following general formula (V):



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.

- 15 6. The manufacturing method according to claim 5, wherein, in the silane compound represented by the general formula (I) and the siloxane compound represented by the general formula (II), R^4 is a glycidoxylalkyl group, an epoxycycloalkylalkyl group, or an oxiranylalkyl group.

- 20 7. The manufacturing method according to claim 5, wherein, in the silane compound represented by the general formula (V), R^3 is a naphthyl group or a naphthyl ethyl group.

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2014/055531

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G77/14 C08L83/06 C08G77/00
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

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
Y	Practical example 2; paragraphs [0061], [0020], [0079], [0100]	1-7

X	US 2012/178022 A1 (KAMOGAWA MASAO [JP] ET AL) 12 July 2012 (2012-07-12)	1-7
Y	synthesis example 8; paragraphs [0023], [0071] paragraphs [0025] - [0026], [0015], [0071]	1-7

Y	"Silicones", 15 April 2003 (2003-04-15), ENCYCLOPEDIA OF POLYMER SCIENCE AND TECHNOLOGY, WILEY, US, PAGE(S) 765 - 841, XP007918236, pages 782-783	5-7



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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

"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

11 April 2014

Date of mailing of the international search report

17/04/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Dalet, Pierre

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/JP2014/055531

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
