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(54) Title: METHOD OF PRODUCING A POLYETHER-MODIFIED ORGANOPOLYSILOXANE

(57) Abstract: To provide an efficient method that uses a safe and convenient procedure to produce, at high purities, an organopolysiloxane having a polyether-modified group bonded to silicon across the Si-O-C bond. The method of producing a polyether-modified organopolysiloxane is characterized by reacting (a) an organohydrogenpolysiloxane with (b) a hydroxy-terminated polyoxyalkylene or hydroxy-terminated polyglycerol in the presence of (c) a platinum-type catalyst and (d) an organic acid.



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DESCRIPTION

Title of Invention

5 METHOD OF PRODUCING A POLYETHER-MODIFIED ORGANOPOLYSILOXANE

Technical Field

[0001] The present invention relates to a method of producing a polyether-modified organopolysiloxane in which a polyether group is bonded to a silicon atom through the
10 Si-O-C bond. This polyether-modified organopolysiloxane is useful as a surfactant and as a raw material for cosmetics.

Background Art

[0002] The alkali metal alkoxide-catalyzed or alkali metal hydroxide-catalyzed dehydrogenation reaction between an alcoholic hydroxyl group-containing polyether
15 compound and, for example, a methylhydrogenpolysiloxane, is already known as a method of producing a polyether-modified organopolysiloxane in which a polyether group is bonded to a silicon atom through the Si-O-C bond (Patent Reference 1 and Patent Reference 2). However, a problem with these reactions has been the occurrence of
20 siloxane chain cleavage during the reaction step due to the use of a strong base as the catalyst, which has made it quite difficult to obtain the high degree of polymerization polyether-modified organopolysiloxane that is useful as a cosmetic starting material.

[0003] Patent Reference 3 describes a method of producing an alkoxy-modified silicone, in which an organohydrogenpolysiloxane and an aliphatic alcohol are reacted in the presence of a platinum-type catalyst acting as a dehydrogenation catalyst and an
25 organic acid acting as a reaction auxiliary. However, there is no disclosure in this patent reference of a polyether-modified organopolysiloxane that has a polyoxyalkylene group

or polyglycerol group bonded to a silicon atom through the Si—O—C bond in side chain position or in terminal position on the molecular chain.

[0004] On the other hand, an organopolysiloxane that has a polyether-modified group bonded to silicon through the Si—O—C bond can be obtained by subjecting the silicon-

5 bonded hydrogen in an organohydrogenpolysiloxane to dehydrogenation and halogenation using allyl chloride or bromine gas and thereafter reacting with a polyether that has a terminal hydroxy group. However, toxicity is a problem here because this reaction is accompanied by the generation of bromine or a hydrogen halide gas; in addition, a crosslinking reaction occurs between the siloxane molecular chains during the
10 reaction process, which has resulted in the side production of a partially crosslinking material.

[0005]

[Patent Reference 1] JP 48-019941 B

[Patent Reference 2] JP 62-036424 A

15 [Patent Reference 3] JP 04-126723 A (JP 2,580,379 B)

Disclosure of Invention

Technical Problems to be Solved

[0006] The present invention seeks to solve the problems described above, and an
20 object of the present invention is to provide an efficient method that uses a safe and convenient procedure to produce, at high purities, an organopolysiloxane that has a polyether-modified group bonded to silicon across the Si—O—C bond.

Solution to Problems

[0007] The aforementioned object is achieved by a method of producing a polyether-
25 modified organopolysiloxane, said method being characterized by reacting (a) an organohydrogenpolysiloxane with (b) a hydroxy-terminated polyoxyalkylene or a

hydroxy-terminated polyglycerol in the presence of (c) a platinum-type catalyst and (d) an organic acid.

[0008] That is, the aforementioned object is achieved by

“[1] A method of producing a polyether-modified organopolysiloxane that has a

5 polyether group bonded to a silicon atom via the Si-O-C bond, said method of producing
a polyether-modified organopolysiloxane being characterized by reacting

(a) an organohydrogenpolysiloxane

with

(b) a hydroxy-terminated polyoxyalkylene or a hydroxy-terminated polyglycerol

10 in the presence of

(c) a platinum-type catalyst and

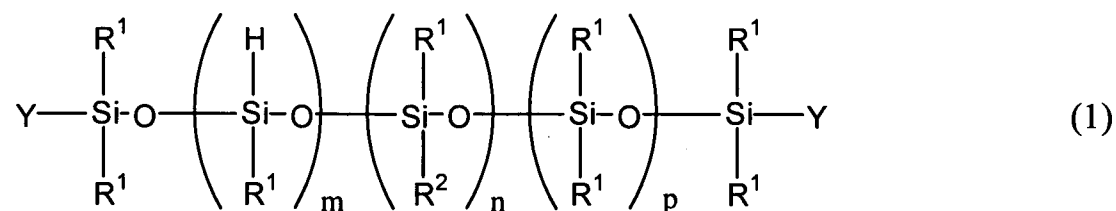
(d) an organic acid.

[2] The method of producing a polyether-modified organopolysiloxane according to [1],

wherein the method is characterized in that the organohydrogenpolysiloxane (a) is a

15 straight-chain or branched-chained organohydrogenpolysiloxane represented by the following general formula (1)

[General formula (1)]:

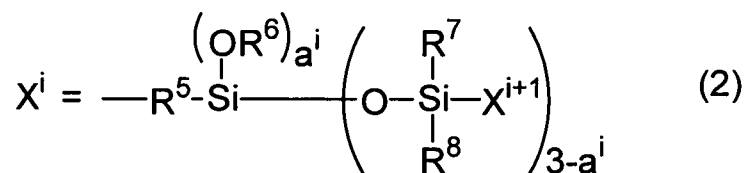


wherein R¹ is a C₁₋₅ monovalent hydrocarbonyl group; R² is an amino group-

20 containing group, a carboxyl group-containing group, a C₆₋₂₀ substituted or unsubstituted monovalent hydrocarbyl group, a functional group represented by -O-Si(R³)₃ wherein R³ is a C₁₋₆ alkyl group or the phenyl group, or a functional group represented by -O-Si(R⁴)₂-X¹ wherein R⁴ is either C₁₋₆ alkyl group or the phenyl

group and when $i = 1$, X^1 is a silylalkyl group represented by the following general formula (2); m , n , and p are each numbers greater than or equal to 0; $(m + n + p)$ is a number in the range from 1 to 1000; each Y is independently a group selected from the hydrogen atom, R^1 , and R^2 ; and when $m = 0$ at least one of Y is the hydrogen atom;

[General formula (2)]:



wherein R^5 is a straight- or branched-chain alkylene group represented by C_rH_{2r} wherein r is an integer from 2 to 20; R^6 is hydrogen atom, C_{1-6} alkyl group, or phenyl group; R^7 and R^8 are selected from hydrogen atom, C_{1-6} alkyl group and phenyl group; i indicates the generation of the silylalkyl group represented by X^i and is an integer from 1 to c where c is the number of generations; the number of generations c is an integer from 1 to 10; a^i is an integer from 0 to 2 when i is 1 and is a number less than 3 when i is 2 or more; and X^{i+1} is the aforementioned silylalkyl group when i is less than c and is the methyl group ($-CH_3$) when $i = c$.

[3] The method of producing a polyether-modified organopolysiloxane according to [1], wherein the method is characterized in that the organic acid (d) is an organic acid that has a carboxyl group or a phenolic hydroxyl group in the molecule.

[4] A cosmetic comprising a polyether-modified organopolysiloxane obtained by the production method according to any of [1] to [3].”

Advantageous Effects of Invention

[0009] The method of the present invention for producing a polyether-modified organopolysiloxane provides an efficient method that uses a safe and convenient procedure to produce, at high purities, an organopolysiloxane that has a polyether-modified group bonded to silicon via the Si—O—C bond.

5 Description of the Invention

[0010] The present invention relates to a method of producing an organopolysiloxane that has a polyether-modified group bonded to silicon via the Si—O—C bond, said method being characterized by reacting (a) an organohydrogenpolysiloxane with (b) a hydroxy-terminated polyoxyalkylene or a hydroxy-terminated polyglycerol in the presence of (c)
10 a platinum-type catalyst and (d) an organic acid. The starting components (a) to (d) and the reaction are described in detail herebelow.

[0011] The organohydrogenpolysiloxane (a) is a straight-chain, cyclic, or branched-chain organohydrogenpolysiloxane that contains silicon-bonded hydrogen in the molecule, and as desired it may be a silicon-type copolymer that contains a C₁₋₂₀
15 divalent hydrocarbyl group or a divalent polyether chain in a portion of the polysiloxane main chain. The silicon-bonded hydrogen may be in terminal or side chain position on the molecular chain or may be in terminal or side chain position on a siloxane chain that branches from the main chain, but its bonding position is not particularly limited. The degree of polymerization of the component (a) organohydrogenpolysiloxane is also not
20 particularly limited, and a component (a) organohydrogenpolysiloxane may be used ranging from organohydrogenpolysiloxane having a degree of polymerization low enough to exhibit volatility to an organohydrogenpolysiloxane having a degree of polymerization high enough to take the gum-like form at room temperature.

[0012] The component (a) organohydrogenpolysiloxane may contain a monovalent
25 organic group in addition to the methyl group and silicon-bonded hydrogen atom. The use of such an organic group-containing organohydrogenpolysiloxane for component (a)

has the advantage of making possible the facile production of a co-modified organopolysiloxane that has a previously introduced organic group in addition to the polyether-modified group bonded to silicon via the Si–O–C bond. The organic group can be introduced beforehand onto the polysiloxane main chain by, for example, an addition
5 reaction in the presence of a hydrosilylation reaction catalyst between a methylhydrogenpolysiloxane and an organic compound that has a carbon-carbon double bond, e.g., the allyl group ($\text{CH}_2=\text{CH CH}_2-$) and so forth.

[0013] This organic group is a known organic group other than the methyl group, the silicon-bonded hydrogen atom, and the polyether-modified group bonded to silicon
10 across the Si–O–C bond that is introduced by the production method of the present invention, and there are no particular restrictions on this organic group as long as it is a functional group as introduced into the modified silicones that are used as, for example, cosmetic starting materials and so forth. Examples of this organic group are phenyl group, C_{6-20} long-chain alkyl group, fluoroalkyl group, fluoropolyether group, alkoxy
15 group, amino group-containing groups, carboxyl group-containing groups, sugar residue-containing groups, the carbinol group, acryloxy-containing groups, the trimethylsiloxy group, the carbosiloxane dendrimer disclosed in JP 2001-213885 A, and so forth.

[0014] An organohydrogenpolysiloxane having a polyether-modified group bonded to silicon across the Si–C bond may also be used as component (a). Such an
20 organohydrogenpolysiloxane can be simply prepared by an addition reaction between a desired methylhydrogenpolysiloxane and a polyoxyalkylene or polyglycerol having the allyl group in terminal position on the molecular chain. The use of such a component (a) in the present invention makes it possible to produce a polyether-modified organopolysiloxane that has two types of polyether-modified groups that differ in the
25 type of linking group bonded to silicon, i.e., a polyether-modified group bonded to

silicon across the Si–C bond and a polyether-modified group bonded to silicon across the Si–O–C bond.

[0015] In addition, the method of the present invention for producing a polyether-modified organopolysiloxane makes it possible to obtain a polyether-modified

organopolysiloxane that to some degree retains the acyloxy group or phenoxy group introduced during the reaction during precursor formation. This acyloxy group or phenoxy group is introduced onto the siloxane chain when the herebelow-described organic acid (d) — particularly an organic acid that has the carboxyl group (–COOH) or a phenolic hydroxyl group (–C₆H₄(OH)) in the molecule — undergoes a

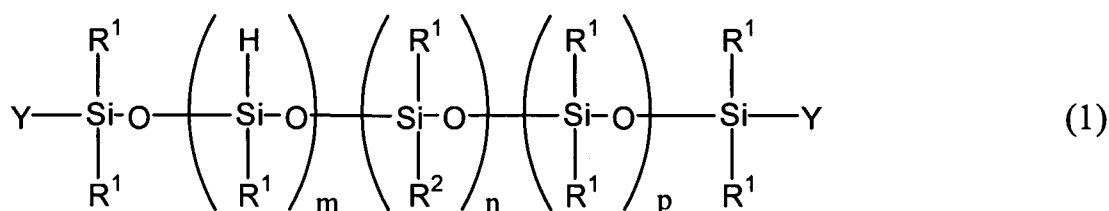
dehydrogenation reaction with the previously described component (a) in the presence of the platinum-type catalyst (c) to form the acyloxysiloxane or phenoxysiloxane that is the reaction precursor. Due to this, a polyether-modified organopolysiloxane that contains unreacted acyloxy or phenoxy groups can be obtained by reacting component (b) in an amount that is less than the introduced acyloxy or phenoxy group in the molar ratio.

[0016] In a particularly preferable embodiment, the component (a)

organohydrogenpolysiloxane is a straight- or branched-chain

organohydrogenpolysiloxane represented by the following general formula (1).

General formula (1):

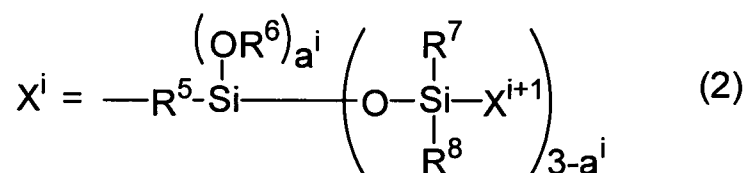


In general formula (1), R¹ is a C₁₋₅ monovalent hydrocarbyl group and preferably is the hydroxyl group or a methyl group. R² is an amino group-containing group; a carboxyl group-containing group; a C₆₋₂₀ substituted or unsubstituted

monovalent hydrocarbyl group such as the phenyl group, tolyl group, cyclohexyl group, a C₆₋₂₀ chain-type alkyl group, and so forth; or a functional group represented by –O–Si(R³)₃ or –O–Si(R⁴)₂–X¹. **m**, **n**, and **p** are each numbers greater than or equal to 0 and (**m** + **n** + **p**) is a number in the range from 1 to 1000. Each Y is independently a group
 5 selected from the hydrogen atom, R¹, and R², wherein when **m** = 0 at least one of Y is the hydrogen atom.

[0018] R³ is C₁₋₆ alkyl group or phenyl group, wherein methyl and phenyl groups are preferred. R⁴ is either C₁₋₆ alkyl or phenyl group and when **i** = 1 X¹ is a silylalkyl group represented by the following general formula (2).

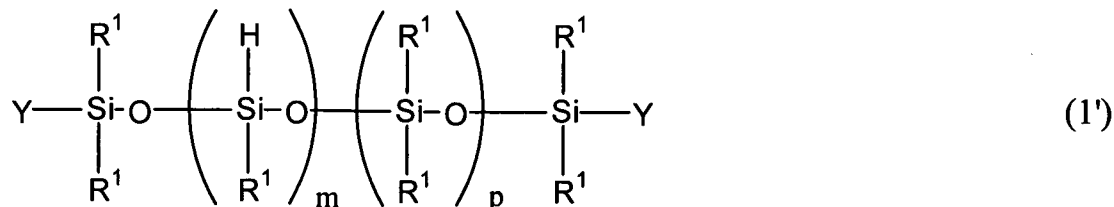
10 General formula (2):



[0019] In general formula (2), R⁵ is a straight- or branched-chain alkylene group represented by C_rH_{2r} wherein **r** is an integer from 2 to 20. R⁶ is hydrogen atom, C₁₋₆ alkyl group, or phenyl group. R⁷ and R⁸ are hydrogen atom, C₁₋₆ alkyl group, or phenyl group. **i** indicates the generation of the silylalkyl group represented by Xⁱ and is an
 15 integer from 1 to **c** where **c** is the number of generations; the number of generations **c** is an integer from 1 to 10; **aⁱ** is an integer from 0 to 2 when **i** is 1 and is a number less than 3 when **i** is 2 or more; and Xⁱ⁺¹ is the aforementioned silylalkyl group when **i** is less than **c** and is the methyl group –CH₃ when **i** = **c**.

[0020] The component (a) organohydrogenpolysiloxane is most preferably the straight-chain organohydrogenpolysiloxane represented by the following general formula (1').

General formula (1'):



5 [0021] In general formula (1'), R^1 is a group as previously defined; m and p are each numbers greater than or equal to 0; and $(m + p)$ is a number in the range from 1 to 1000. Each Y is independently a group selected from the hydrogen atom and R^1 , wherein when $m = 0$ at least one of Y is hydrogen atom. More preferably, m is a number in the range from 0 to 200 and p is a number in the range from 10 to 500. Most preferably, m is a
10 number in the range from 1 to 20 and p is a number in the range from 15 to 50.

[0022] Component (b) is a hydroxy-terminated polyoxyalkylene or a hydroxy-terminated polyglycerol, and it is this component that forms the polyether-modified group that is bonded to silicon across the Si-O-C bond. Here, hydroxy-terminated denotes the presence of the hydroxy group (-OH) at the end of the molecular chain of the
15 aforementioned polyether compound and does not refer to hydroxyl present in the polyether chain structure. The said polyether compound may be a molecular of straight chain or branched chain, and may be a polyether compound that has dendritic branching through a trivalent linking group. It may also be a polyether compound in which a polyglycerol chain moiety and a polyoxyalkylene chain moiety are bonded within the
20 same molecule in a block or random sequence.

[0023] The straight-chain hydroxy-terminated polyoxyalkylenes and hydroxy-terminated polyglycerols represented by the following structural formulas (3), (4) and (5) are examples of preferred and easy-to-acquire component (b)'s.

structural formula (3): $R^9-(O-R^{10})_r-R^{11}-OH$

5 structural formula (4): $R^9-(OCH(CH_2OH)CH_2)_s-R^{11}-OH$

structural formula (5): $R^9-(OCH_2CH(OH)CH_2)_s-R^{11}-OH$

[0024] In the preceding formulas, R^9 is hydrogen atom or C_{1-30} monovalent hydrocarbyl group, wherein the hydrogen atom and C_{1-20} alkyl are preferred. Each R^{10} is independently C_{1-10} alkylene group or C_{6-10} arylene group. When the obtained
10 polyether-modified organopolysiloxane is used as a cosmetic raw material or as a surfactant, R^{10} is particularly preferably an alkylene group selected from ethylene, propylene, and butylene. R^{11} is a freely selectable linking group between the polyether chain and the terminal hydroxy group and is an optional divalent organic group. In
suitable embodiments, the linking group R^{11} is not present or R^{11} is a C_{1-20} oxyalkylene
15 group $-OC_nH_{2n}-$, wherein n is a number in the range from 1 to 20, C_{1-20} alkylene group, C_{1-20} divalent hydrocarbyl group, or C_{6-20} arylene group. r is a number from 1 to 50 and particularly preferably is 3 to 30 and most preferably is 5 to 20. s is a number from 1 to 50 and particularly preferably is 1 to 20 and most preferably is 1 to 10.

[0025] The platinum-type catalyst (c) functions as a catalyst of the reaction that forms
20 the acyloxysiloxane or phenoxysiloxane by a dehydrogenation reaction in the presence of the organic acid (d), vide infra, between the organohydrogenpolysiloxane and the organic acid and that then introduces the polyether-modified group bonded to silicon via the Si-

O–C bond into the organopolysiloxane by an exchange reaction between the acyloxysiloxane or phenoxysiloxane and the hydroxy-terminated polyoxyalkylene or hydroxy-terminated polyglycerol.

[0026] The platinum-type catalyst used can be exemplified by transition metal complex

5 compounds of platinum, palladium, rhodium, ruthenium, cobalt, nickel, and so forth.

Examples of preferred platinum-type catalysts (c) are rhodium compounds, palladium compounds, chloroplatinic acid, alcohol-modified chloroplatinic acid, olefin complexes of chloroplatinic acid, chloroplatinic acid/ketone complexes, chloroplatinic

acid/vinylsiloxane complexes, platinum tetrachloride, finely divided platinum, solid

10 platinum supported on a carrier such as alumina or silica, platinum black, olefin

complexes of platinum, alkenylsiloxane complexes of platinum, carbonyl complexes of

platinum, and a thermoplastic organic resin powder, e.g., of a methyl methacrylate resin,

polycarbonate resin, polystyrene resin, silicone resin, and so forth, that contains a

platinum-type catalyst as described above.

15 [0027] This platinum-type catalyst (c) is used in a so-called catalytic quantity. In

specific terms it is used in the range from 1 to 1,000 ppm and preferably in the range

from 5 to 200 ppm, in each case as the amount (weight) of platinum group metal with reference to component (a).

[0028] The organic acid (d) is a component required for the formation of the

20 acyloxysiloxane or phenoxysiloxane reaction precursor by the dehydrogenation reaction between an organic acid and the organohydrogenpolysiloxane in the presence of

component (c). There are no particular limitations on this organic acid as long as it is an organic acid that can form a reactive acyloxy group or phenoxy group after the

dehydrogenation reaction, but an organic acid that has the carboxyl group (–COOH) or a

25 phenolic hydroxyl group (–C₆H₄(OH)) in the molecule is preferred. More specific

examples are formic acid, acetic acid, propionic acid, butyric acid, oxalic acid, citric

acid, benzoic acid, and phenol. Acetic acid is particularly preferred in the viewpoints of the ease of acquisition and the ease of blending in the case of use as a cosmetic raw material.

[0029] A solvent may be used as an optional components in the method of the present invention for producing a polyether-modified organopolysiloxane, and when a solvent is used it should not contain active hydrogen. Given this, one or two or more solvents selected from the following can be used, although there is no particular limitation to the following: aliphatic hydrocarbons such as hexane, heptane, and so forth; aromatic hydrocarbons such as toluene, xylene, and so forth; ester and ether compounds such as ethyl acetate, dibutyl ether, and so forth; chlorinated solvents such as trichloroethylene, trichloroethane, and so forth; and branched hydrocarbons such as α -olefins and so forth.

[0030] The method of the present invention for producing a polyether-modified organopolysiloxane can provide a polyether-modified organopolysiloxane having a polyether-modified group bonded to silicon across the Si-O-C bond, by adding the organic acid (d) to the organohydrogenpolysiloxane (a) and running a dehydrogenation reaction in the presence of the platinum-type catalyst (c) and subsequently adding the hydroxy-terminated polyoxyalkylene or hydroxy-terminated polyglycerol (b) and running an exchange reaction.

[0031] With the goal of simplifying production, a procedure may be selected in which [1] the reaction is carried out by preparing a mixture of solvent and components (b), (c) and (d) and adding the organohydrogenpolysiloxane (a) dropwise to this mixture or [2] the reaction is carried out by preparing a mixture of solvent and components (a), (b), and (c) and adding the organic acid (d) dropwise to this mixture.

[0032] The quantity of reaction of the hydroxy-terminated polyoxyalkylene or hydroxy-terminated polyglycerol (b) may be freely adjusted in the production method of the present invention accordance with the modification rate, but the use of 1.0 equivalent to

2.0 equivalents as the amount of substance ratio with reference to the silicon-bonded hydrogen in the organohydrogenpolysiloxane (a) is particularly suitable while the use of 1.0 equivalent to 1.3 equivalents as the amount of molar ratio with reference to the silicon-bonded hydrogen in the organohydrogenpolysiloxane (a) is most suitable.

5 **[0033]** The organic acid (d) is added in a quantity sufficient for the acyloxylation by the dehydrogenation reaction of the silicon-bonded hydrogen in component (a); however, it need not be added in an equivalent amount because the organic acid (d) is regenerated after the exchange reaction with component (b). However, viewed from the perspective of promoting the reaction, a preferred quantity of addition is at least 1.0 equivalent in
10 molar ratio with reference to the silicon-bonded hydrogen in the organohydrogenpolysiloxane (a), while from the standpoint of promoting the exchange reaction the quantity of organic acid (d) is particularly preferably added in the range from 1.1 to 1.5 equivalents in molar ratio with reference to the silicon-bonded hydrogen in component (a).

15 **[0034]** The dehydrogenation and exchange reactions of the organohydrogenpolysiloxane (a) proceed in the range from room temperature to 200°C. However, due to the slow reaction rate at 50°C and below, the dehydrogenation reaction of component (a) and the reaction with the organic acid (d) are preferably run under 70 to 120°C and are particularly preferably run under 80°C to 110°C. After the reaction
20 with the organic acid, the exchange reaction with component (b) is preferably run under 120 to 180°C and is particularly preferably run under 130 to 170°C.

25 **[0035]** The reaction time varies as a function of the amount of use of the organic acid (d) and the quantities of introduction of the starting materials, but when a reaction temperature is selected as described above, the polyether-modified organopolysiloxane having a polyether-modified group bonded across the Si—O—C bond to silicon can be obtained by a reaction for 1 hour to 20 hours. The point of completion for the

dehydrogenation reaction of component (a) and its reaction with the organic acid (d) and the point of completion for the exchange reaction with component (b) can be easily checked using the infrared absorption spectrum (IR) or the ^{13}C - or ^{29}Si -NMR.

[0036] After the completion of the reaction, the target polyether-modified

organopolysiloxane having a polyether-modified group bonded to silicon across the Si-O-C bond can be obtained by washing the reaction product containing the polyether-modified organopolysiloxane with water to remove the organic acid and as necessary distilling off the solvent under reduced pressure. The organic acid and solvent may also be removed without a water wash by distillation of the reaction product under reduced pressure. However, when the component (b) added in excess amount and has a high boiling point, its removal under reduced pressure conditions may not be possible; even in such case, the corresponding mixture can be used as a surfactant or as a cosmetic raw material.

Examples

[0037] Examples and comparative examples are provided below in order to specifically describe the present invention, but the present invention is not limited to these examples. In the following examples, parts denotes mass parts in all instances and Me represents the methyl group. The viscosity is the value measured at 25°C. The compounds in the examples and comparative examples were identified by the infrared absorption spectrum (IR) and ^{13}C - and ^{29}Si -NMR using the following instrumentation and methodologies.

[0038]

[The infrared absorption spectrum]

The silicon-bonded hydrogen atom was quantitated in the examples using an FT/IR-4100 Fourier-transform infrared spectrophotometer (from the JASCO Corporation) based on the absorption intensity of the characteristic absorption peak at the absorption wavelength of 2180 cm^{-1} assigned to the silicon-bonded hydrogen atom.

[NMR analysis]

The chemical structure was identified in the examples using the following ^{13}C - and ^{29}Si -NMR analyses.

NMR instrument: JEOL JNM-EX400 (from JEOL Ltd.) Fourier-transform nuclear
5 magnetic resonance spectrometer

Identification method: The peak analysis values were calculated for the signals
originating from the ^{13}C and ^{29}Si in the different siloxane units as described below. The
average structural formula was identified by determining the constituent ratios for the
individual siloxane units and carbon units based on a determination of the ratios of the
10 integrated values for these individual siloxane units and carbon units.

< Siloxane units: position of signals originating from ^{29}Si >

$\text{Me}_3\text{SiO}_{1/2}$: around 7.5 ppm

$\text{Me}_2\text{SiO}_{2/2}$: around -21 to -22 ppm

$\text{MeSiO}_{2/2}$: around -59.4 ppm
15 OCH

$\text{MeSiO}_{2/2}$: around -59.9 ppm
 OC(O)CH_3

$\text{MeHSiO}_{2/2}$: around -37.1 ppm

$\text{MeClSiO}_{2/2}$: around -45.6 ppm

20 < Carbon units: positions of signals originating from ^{13}C >

SiCH_3 : around 2.0 to -2.6 ppm

OCH : around 76 to 70 ppm

CCH_2 : around 32 to 13 ppm

OC(O) : around 169 ppm

OC(O)CH₃: around 22.6 ppm

[0039] [Practical Example 1]

[1] The following starting materials were introduced into a separable flask equipped with a thermometer, condenser, and stirrer and were stirred for 30 minutes while heating.

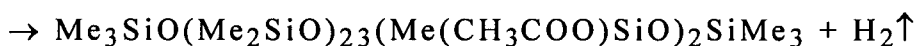
(a) 66.3 g of methylhydrogenpolysiloxane represented by the following structural formula

structural formula: $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_{23}(\text{MeHSiO})_2\text{SiMe}_3$

(c) 0.0003 g of platinum-type catalyst (divinyltetradisiloxane complex of platinum)

(d) 5.0 g of acetic acid

[2] After the temperature had been raised to 90°C, 10 g of said mixture was taken out and the infrared absorption spectrum (IR) of the reaction solution was measured after stirring for 4 hours; the peak originating with the silicon-bonded hydrogen atom was found to be extinguished (refer to the following reaction equation).
reaction equation:



[3] The following starting material was introduced and the temperature was raised to 144°C, after which stirring was continued for 2 hours.

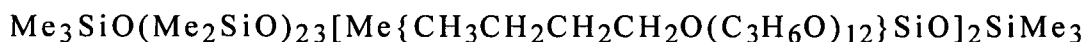
(b) 55.9 g of hydroxy-terminated polyoxyalkylene represented by the following structural formula

structural formula: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{C}_3\text{H}_6\text{O})_{12}\text{H}$

[4] While stripping under reduced pressure, the exchange reaction was continued for an additional 8 hours at 148°C while stirring to produce the polyether-modified

organopolysiloxane having a polyether-modified group bonded to silicon across the Si-O-C bond; this polyether-modified organopolysiloxane had the structural formula given below. According to the results of measurement by ^{13}C - and ^{29}Si -NMR, the presence of other by-products, e.g., crosslinked materials and so forth, was not observed.

structural formula:



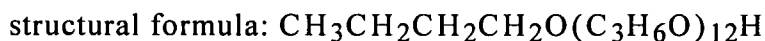
[0040] [Comparative Example 1]

[1] The following starting materials were introduced into a separable flask equipped with a thermometer, condenser, and stirrer and were stirred for 2 hours after heating to 144°C. While stripping under reduced pressure, the exchange reaction was continued for an additional 8 hours at 148°C while stirring to obtain a reaction product.

(a) 54.6 g of methylhydrogenpolysiloxane represented by the following structural formula



(b) 54.5 g of hydroxy-terminated polyoxyalkylene represented by the following structural formula



(c) 0.01 g of platinum-type catalyst (divinyltetradisiloxane complex of platinum)

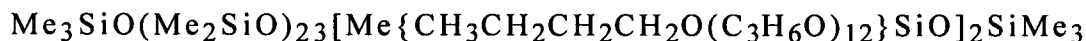
[2] When the infrared absorption spectrum (IR) of this reaction solution was measured, it was found that at least 50% of the peak originating with the silicon-bonded hydrogen atom remained and the exchange reaction was therefore not completed. Thus, only a mixture of the starting methylhydrogenpolysiloxane and

the polyether-modified organopolysiloxane having a polyether-modified group bonded to silicon across the Si—O—C bond could be obtained.

[0041] [Comparative Example 2]

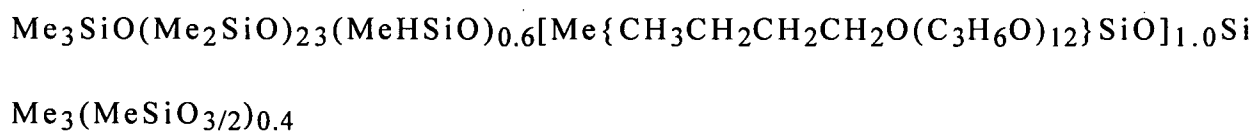
The procedure of Example 1 was followed, but using 9.5 g of (d') chloroform CHCl_3 in place of the 5.0 g of (d) acetic acid, to obtain a reaction solution containing a polyether-modified organopolysiloxane having a polyether-modified group bonded to silicon across the Si—O—C bond; this polyether-modified organopolysiloxane had the structural formula given below. Dichloromethane CH_2Cl_2 was produced as a by-product in the reaction process.

10 structural formula:



[0042] When the infrared absorption spectrum (IR) of this reaction solution was measured, it was found that at least 30% of the peak originating with the silicon-bonded hydrogen atom remained and the exchange reaction was therefore not completed. The results of ^{13}C - and ^{29}Si -NMR measurements demonstrated that the reaction solution contained a by-product with the structural formula given below, which had an intermolecular crosslinked structure.

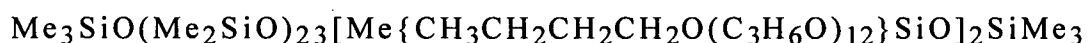
structural formula:



[0043] [Comparative Example 3]

The procedure of Example 1 was followed, but using 9.3 g of (d'') allyl bromide $\text{CH}_2=\text{CHCH}_2\text{Br}$ in place of the 5.0 g of (d) acetic acid, to obtain a reaction solution containing a polyether-modified organopolysiloxane having a polyether-modified group bonded to silicon across the Si-O-C bond; this polyether-modified organopolysiloxane had the structural formula given below.

structural formula:



[0044] When the infrared absorption spectrum (IR) of this reaction solution was measured, it was found that at least 85% of the peak originating with the silicon-bonded hydrogen atom remained and the exchange reaction was therefore not completed. Thus, only a mixture of the starting methylhydrogenpolysiloxane and the polyether-modified organopolysiloxane having a polyether-modified group bonded to silicon across the Si-O-C bond could be obtained.

[0045] [Comparative Example 4]

The procedure of Example 1 was followed, but in this case carrying out the dehydrogenation reaction and bromination of the silicon-bonded hydrogen moiety at 10°C or below during the dropwise addition of 11.2 g of (d''') bromine Br₂ in place of said 5.0 g of (d) acetic acid, to obtain a reaction solution containing a polyether-

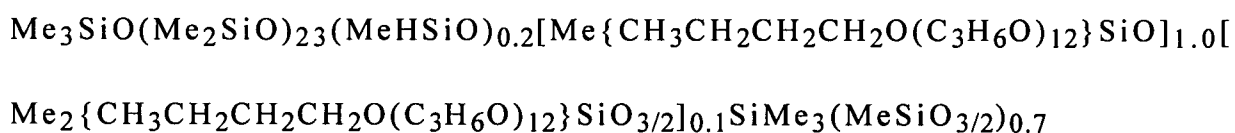
5 modified organopolysiloxane having a polyether-modified group bonded to silicon across the Si—O—C bond; this polyether-modified organopolysiloxane had the structural formula given below. Toxic hydrogen bromide gas was produced as a by-product in this reaction process.

structural formula:



[0046] Measurement of the infrared absorption spectrum (IR) on this reaction solution showed that the peak originating with silicon-bonded hydrogen was almost completely extinguished. However, according to the results of ¹³C- and ²⁹Si-NMR measurements, the reaction solution contained not only the straight-chain polyether-modified

15 organopolysiloxane with the structural formula given above, but also the by-product with the structural formula given below, which had an intermolecular crosslinked structure.



[0047] The results obtained in Example 1 and Comparative Examples 1 to 4 are

20 reported in Table 1. The production method according to the invention of this application (cf. Example 1) makes possible the safe, simple, and convenient production of a polyether-modified organopolysiloxane having a polyether-modified group bonded to silicon across the Si—O—C bond, and, because the obtained polyether-modified organopolysiloxane does not contain by-products such as crosslinked material and so

25 forth, it also makes possible an efficient and high purity production.

[0048] [Table 1.]

example	component corresponding to component (d)	quantity of residual SiH (%)	Did secondary production of crosslinked material occur?	by-product
Example 1	(d) acetic acid	0% — the reaction went to completion	no	hydrogen
Comparative Example 1	none	50% — the reaction did not go to completion	no	hydrogen
Comparative Example 2	(d') chloroform	30% — the reaction did not go to completion	yes	dichloromethane
Comparative Example 3	(d'') allyl bromide	85% — the reaction did not go to completion	no	—
Comparative Example 4	(d''') bromine	0% — the reaction was almost complete	yes	hydrogen bromide

[0049] [Industrial Applicability]

5 The production method of the present invention makes it possible to easily obtain a polyether-modified organopolysiloxane that has a polyether-modified group bonded to silicon across the Si—O—C bond and also makes it possible to obtain a polyether-modified organopolysiloxane that has two or more modifying groups whereby the aforementioned polyether-modified group is introduced in combination with another organic group or

10 groups. The obtained polyether-modified organopolysiloxane exhibits high purity and is very useful as a surfactant — including emulsifying agents and dispersing agents — and as a raw material for cosmetics. This polyether-modified organopolysiloxane is similarly useful as a foam adjustment agent, a defoamer, a fiber treatment agent, a cosmetic component, a component for topical drug preparations, and so forth. Moreover, its

15 applications are not specifically limited to the heretofore known applications of polyether-modified organopolysiloxanes, and it may be used by incorporation into, for example, emulsions for industrial applications and cosmetic applications.

CLAIMS

1. A method of producing a polyether-modified organopolysiloxane that has a polyether group bonded to a silicon atom via the Si-O-C bond, said method of producing a polyether-modified organopolysiloxane being characterized by reacting

(a) an organohydrogenpolysiloxane

with

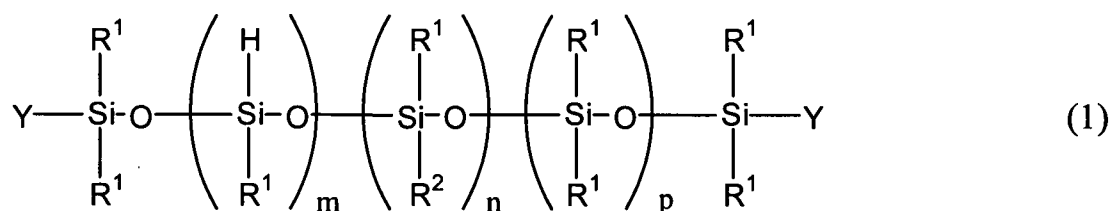
(b) a hydroxy-terminated polyoxyalkylene or a hydroxy-terminated polyglycerol

in the presence of (c) a platinum-type catalyst and

(d) an organic acid.

2. The method of producing a polyether-modified organopolysiloxane according to claim 1, wherein the method is characterized in that the organohydrogenpolysiloxane (a) is a straight-chain or branched-chained organohydrogenpolysiloxane represented by the following general formula (1)

[General formula (1)]:



wherein R^1 is a C_{1-5} monovalent hydrocarbyl group; R^2 is an amino group-

containing group, a carboxyl group-containing group, a C_{6-20} substituted or

unsubstituted monovalent hydrocarbyl group, a functional group represented by $-\text{O}-$

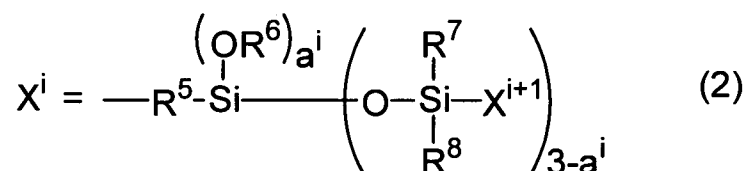
$\text{Si}(\text{R}^3)_3$ wherein R^3 is a C_{1-6} alkyl group or the phenyl group, or a functional group

represented by $-\text{O}-\text{Si}(\text{R}^4)_2-\text{X}^1$ wherein R^4 is either C_{1-6} alkyl group or the phenyl

group and when $i = 1$, X^1 is a silylalkyl group represented by the following general

formula (2); m , n , and p are each numbers greater than or equal to 0; $(m + n + p)$ is a number in the range from 1 to 1000; each Y is independently a group selected from the hydrogen atom, R^1 , and R^2 ; and when $m = 0$ at least one of Y is the hydrogen atom;

[General formula (2)]:



wherein R^5 is a straight- or branched-chain alkylene group represented by C_rH_{2r}

wherein r is an integer from 2 to 20; R^6 is hydrogen atom, C_{1-6} alkyl group, or

phenyl group; R^7 and R^8 are selected from hydrogen atom, C_{1-6} alkyl group and

phenyl group; i indicates the generation of the silylalkyl group represented by X^i

and is an integer from 1 to c where c is the number of generations; the number of

generations c is an integer from 1 to 10; a^i is an integer from 0 to 2 when i is 1 and

is a number less than 3 when i is 2 or more; and X^{i+1} is the aforementioned

silylalkyl group when i is less than c and is the methyl group ($-CH_3$) when $i = c$.

3. The method of producing a polyether-modified organopolysiloxane

according to claim 1, wherein the method is characterized in that the organic acid (d) is an organic acid that has a carboxyl group or a phenolic hydroxyl group in the molecule.

4. A cosmetic comprising a polyether-modified organopolysiloxane obtained by the production method according to any of claims 1 to 3.

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2010/060411

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G77/46 C08L83/12 A61K8/894
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 A61K

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 practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1 460 098 A1 (GOLDSCHMIDT AG TH [DE] GOLDSCHMIDT GMBH [DE]) 22 September 2004 (2004-09-22) claims 1-5,17	1-4
Y	EP 0 475 440 A2 (SHINETSU CHEMICAL CO [JP]) 18 March 1992 (1992-03-18) claim 1	1-4
A	WO 2009/065644 A1 (EVONIK GOLDSCHMIDT GMBH [DE]; HENNING FRAUKE [DE]; KNOTT WILFRIED [DE]) 28 May 2009 (2009-05-28) claims 13-15	1-4

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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

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Date of the actual completion of the international search

21 September 2010

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/JP2010/060411

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