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(54) Title: POLYORGANOSILOXANE COMPOSITION

(57) Abstract: A polyorganosiloxane composition contains: (A) an alkenyl-functional polyorganosiloxane having an average of at least two alkenyl groups per molecule; and (B) an adduct of (i) an alkali metal compound with (ii) an additive, wherein the additive (ii) is selected from the group consisting of (b1) a bis (triorganosilyl) dicarboxylate of formula (B-I), (b2) a tris (triorganosilyl) phosphite of formula (B-II), and mixtures thereof. The polyorganosiloxane composition shows improved thermal stability.



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POLYORGANOSILOXANE COMPOSITION

FIELD

The present invention relates to a polyorganosiloxane composition and a method of preparing the composition with improved thermal stability.

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INTRODUCTION

Polyorganosiloxanes are widely used in preparing silicone rubbers, adhesives, sealants, and encapsulants. Many applications require these silicone materials be stable when exposed to high temperatures (e.g., 100 degrees Celsius (°C) or higher). A typical process for making alkenyl-functional polyorganosiloxanes involves a ring opening polymerization reaction of cyclic polydiorganosiloxanes such as octamethylcyclotetrasiloxane (also known as “D₄”) and then end capping using a low molecular weight alkenyl-terminated polyorganosiloxane. The ring opening reaction is catalyzed by a base catalyst such as potassium silanolate or potassium hydroxide at a temperature above 100 °C. The product of this base catalyzed reaction is typically an equilibrium mixture comprising as a major portion of linear polyorganosiloxanes and as a minor portion of cyclic polydiorganosiloxanes. The presence of the cyclic polydiorganosiloxanes in the product is undesirable and, therefore, these cyclics are typically removed by a stripping process conducted at high temperatures (e.g., 120 °C or higher) under vacuum. The base catalyst needs to be further treated, e.g., neutralized, to prevent the obtained polyorganosiloxanes from depolymerizing into cyclic polydiorganosiloxanes including D₄, decamethylcyclopentasiloxane (also known as “D₅”), and dodecamethylcyclohexasiloxane (also known as “D₆”) during the stripping process. Moreover, the obtained polyorganosiloxanes and compositions comprising thereof tend to have compromised thermal stability when the base catalyst is not sufficiently neutralized.

Various methods of stabilizing or neutralizing the base catalysts in alkenyl-functional polyorganosiloxanes have been used, such as specific solid organic acids at a molten state during neutralization while forming insoluble adduct with catalysts, organic carboxylic acids of general formula ZCOOH where Z is a hydrocarbon group, silyl phosphates, and silyl phosphonates such as bis(trimethylsilyl) vinylphosphonate. However, the methods of the above prior art suffer from various disadvantages. The method using the solid organic acids requires additional processing steps to separate the insoluble adduct and the residual solid organic acid from the polyorganosiloxane mixture. Some polyorganosiloxane compositions obtained by using neutralizers such as silyl phosphates and silyl phosphonates still give undesirably high mounts of cyclic polydiorganosiloxanes, when subject to high-temperature treatment such as striping. The salts formed from neutralization reaction may also have limited compatibility with alkenyl-functional polyorganosiloxanes. Sometimes white precipitate was observed in the obtained

polyorganosiloxane compositions, which will lead to clarity issues in downstream products. Such issue may limit the use of these polyorganosiloxane compositions in applications such as optically clear resin (OCR) or display encapsulation films where high clarity is required.

There remains a need to identify an additive that can be used to stabilize mixtures comprising an alkenyl-functional polyorganosiloxane and an alkali metal compound and therefore to provide a polyorganosiloxane composition with improved thermal stability and/or clarity.

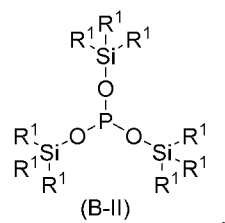
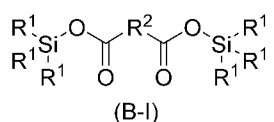
SUMMARY

The present invention provides a novel thermally stable polyorganosiloxane composition (also referred to as “composition”) comprising (A) an alkenyl-functional polyorganosiloxane and (B) an adduct of (i) an alkali metal compound with (ii) a specific additive selected from (b1) a bis(triorganosilyl) dicarboxylate of formula (B-I) herein below, (b2) a tris(triorganosilyl) phosphite of formula (B-II) herein below, or mixtures thereof. The polyorganosiloxane composition shows improved thermal stability as indicated by reduced amounts cyclic siloxanes. Such polyorganosiloxane composition can be prepared by a method comprising the step of: contacting the specific additive (ii) with a mixture comprising the alkenyl-functional polyorganosiloxane and the alkali metal compound (i).

In a first aspect, the present invention is a polyorganosiloxane composition comprising:

(A) an alkenyl-functional polyorganosiloxane having an average of at least two alkenyl groups per molecule; and

(B) an adduct of (i) an alkali metal compound with (ii) an additive, wherein the additive (ii) is selected from the group consisting of (b1) a bis(triorganosilyl) dicarboxylate of formula (B-I), (b2) a tris(triorganosilyl) phosphite of formula (B-II), and mixtures thereof;



where each R^1 is independently a monovalent hydrocarbon group having from 1 to 12 carbon atoms or a monovalent halogenated hydrocarbon group having from 1 to 12 carbon atoms, and R^2 is a single carbon-carbon bond or a divalent hydrocarbon group having 1 to 12 carbon atoms.

In a second aspect, the present invention is a method of preparing the polyorganosiloxane composition of the first aspect. The method comprises the steps of:

a) contacting a mixture comprising the alkenyl-functional polyorganosiloxane (A) and the alkali metal compound (i) with the additive (ii), and optionally,

5 b) stripping the neutralized mixture obtained from step a).

DETAILED DESCRIPTION

Test methods refer to the most recent test method as of the priority date of this document when a date is not indicated with the test method number. References to test methods contain both a reference to the testing society and the test method number. The following test method
10 abbreviations and identifiers apply herein: ASTM refers to ASTM International methods and ISO refers to International Organization for Standards.

Products identified by their tradename refer to the compositions available under those tradenames on the priority date of this document.

“And/or” means “and, or as an alternative”. All ranges include endpoints unless otherwise
15 indicated.

Unless otherwise stated, all weight-percent (wt%) values are relative to the weight of component (A) described herein below.

The polyorganosiloxane composition of the present invention comprises (A) one or more alkenyl-functional polyorganosiloxanes (“component (A)”). The alkenyl-functional
20 polyorganosiloxane (A) useful in the present invention has an average of two or more alkenyl groups per molecule. “Alkenyl” means a branched or unbranched, monovalent hydrocarbon group having one or more carbon-carbon double bonds. The alkenyl group may have 2 to 12 carbon atoms, and can have from 2 to 8 carbon atoms, from 2 to 6 carbon atoms, or from 2 to 4 carbon atoms. Suitable alkenyl groups may include vinyl, allyl, butenyl, and hexenyl. The alkenyl groups
25 can be terminal, pendant, or a combination of both terminal and pendant. “Terminal” groups are on end siloxane groups of a molecule. “End” siloxane groups are attached to only one other siloxane group. “Pendant” groups are on interior siloxane group – siloxane groups bound to at least two other siloxane groups – of the molecule. “Siloxane group” is a group containing SiO that is bound to another Si through the oxygen of the SiO. The alkenyl-functional polyorganosiloxane
30 for component (A) can be a linear structure, partially branched linear structure, branched structure, cyclic structure, network structure, and dendritic structure. Generally, the alkenyl-functional polyorganosiloxane can comprise repeating units described by formula $-(R^M_2SiO)_n$, where each R^M is as described below.

The alkenyl-functional polyorganosiloxane (A) useful in the present invention may have

an average chemical structure (A-I):



where each R^M is independently an alkyl group having 1 to 6 carbon atoms or an aryl group having 6 to 12 carbon atoms, each R' is independently an alkenyl group having 2 to 12 carbon atoms, subscript $a \geq 0$, subscript $b \geq 0$, subscript c is 0 or 1, subscript d is 0 or 1, $(a+b)$ is in a range of from 20 to 10000, and $(a+c+d) \geq 2$.

“Alkyl” means a cyclic, branched, or unbranched, saturated monovalent hydrocarbon group. Suitable alkyl groups for R^M may include, for example, methyl, ethyl, propyl (e.g., isopropyl and/or n-propyl), butyl (e.g., isobutyl, n-butyl, tert-butyl, and/or sec-butyl), pentyl (e.g., isopentyl, neopentyl, and/or tert-pentyl), hexyl, as well as branched saturated hydrocarbon groups of 6 carbon atoms. “Aryl” means a group containing a cyclic, fully unsaturated, hydrocarbon group. Suitable aryl groups for R^M are exemplified by phenyl, tolyl, xylyl, naphthyl, benzyl, and dimethyl phenyl. Each R^M may be the same or different. Each R^M can be an alkyl group. Desirably, each R^M is independently methyl, ethyl, or propyl, more desirably, each R^M is methyl.

Suitable alkenyl groups for R' are as described above, particularly, vinyl, allyl, butenyl, and hexenyl. Each R' may be the same or different. Desirably, each R' is independently vinyl or hexenyl. More desirably, each R' is vinyl.

Subscript a is the average number of $(R'R^MSiO)$ groups per molecule. Subscript b is the average number of (R^M_2SiO) groups per molecule.

The quantity $(a+c+d)$ is 2 or more, even 3 or more while at the same time is typically 30 or less, and can be 20 or less, 10 or less, or even 3 or less. Desirably, subscript a is 0, subscript c is 1, subscript d is 1, and each R^M is methyl. The polyorganosiloxane for component (A) may comprise, or can consist of, one or more than one vinyl dimethyl siloxy-terminated polydimethyl polysiloxane.

The quantity of $(a+b)$ may be in a range of from 20 to 10000, from 20 to 5000, from 20 to 2000, from 25 to 1000, or from 30 to 200. Alternatively, the quantity of $(a+b)$ has a value sufficient to impart the polyorganosiloxane a viscosity at 25 °C of from 10 milliPascal*seconds (mPa·s) to 100,000 mPa·s, and can be from 50 mPa·s to 90,000 mPa·s, from 100 mPa·s to 80,000 mPa·s, or from 200 mPa·s to 70,000 mPa·s. Viscosity can be measured according to ASTM D1084 using a rotational viscometer such as a Brookfield viscometer DV-II at 25 degrees Celsius (°C), unless otherwise stated.

The alkenyl-functional polyorganosiloxane (A) useful in the present invention may comprise one polyorganosiloxane of formula (A-I) or a combination of two or more polyorganosiloxanes of formula (A-I) that may differ in one or more properties such as viscosity,

molecular weight, structure, siloxane units and sequence. When the alkenyl-functional polyorganosiloxane comprises a combination of more than one alkenyl-functional polyorganosiloxane then the viscosity is the combined viscosity of alkenyl-functional polyorganosiloxanes. Suitable alkenyl-functional polyorganosiloxanes may include, for example,

- 5 i) dimethylvinylsiloxyl-terminated polydimethylsiloxane, ii) dimethylvinylsiloxyl-terminated poly(dimethylsiloxane/methylvinylsiloxane), iii) dimethylvinylsiloxyl-terminated polymethylvinylsiloxane, iv) trimethylsiloxyl-terminated poly(dimethylsiloxane/methylvinylsiloxane), v) trimethylsiloxyl-terminated polymethylvinylsiloxane, vi) dimethylvinylsiloxyl-terminated
 10 poly(dimethylsiloxane/methylvinylsiloxane), vii) dimethylvinylsiloxyl-terminated poly(dimethylsiloxane/methylphenylsiloxane), viii) dimethylvinylsiloxyl-terminated poly(dimethylsiloxane/diphenylsiloxane), ix) phenyl,methyl,vinyl-siloxyl-terminated polydimethylsiloxane, x) dimethylhexenylsiloxyl-terminated polydimethylsiloxane, or mixtures thereof. Desirably, the alkenyl-functional polyorganosiloxane of formula (A-I) is bis-
 15 vinyldimethylsiloxyl-terminated polydimethylsiloxane.

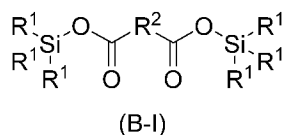
Typically, the amount of the alkenyl-functional polyorganosiloxane (A) in the polyorganosiloxane composition may be greater than 95 wt%, and can be 96 wt% or more, 97 wt% or more, 98 wt% or more, or even 99 wt% or more, based on the total weight of the polyorganosiloxane composition.

- 20 The polyorganosiloxane composition of the present invention also comprises component (B) an adduct of (i) an alkali metal compound with (ii) an additive.

The alkali metal compound (i) useful in the present invention herein refers to a compound that can catalyze ring opening polymerization of cyclic polydiorganosiloxanes. The alkali metal compound can be an alkali metal hydroxide, an alkali metal silanolate, or mixtures thereof.

- 25 Suitable alkali metal hydroxides may include, for example, potassium hydroxide, sodium hydroxide, lithium hydroxide, cesium hydroxide, calcium hydroxide, magnesium hydroxide, or mixtures thereof. Suitable alkali metal silanolates may include, for example, potassium silanolate, sodium silanolate, lithium silanolate, cesium silanolate, calcium silanolate, magnesium silanolate, or mixtures thereof. Desirably, the alkali metal compound is selected from the group consisting of
 30 a potassium hydroxide, a potassium silanolate, and mixtures thereof.

The additive (ii) useful in the present invention is selected from the group consisting of (b1) bis(triorganosilyl) dicarboxylate of formula (B-I) below, (b2) a tris(triorganosilyl) phosphite of formula (B-II) below, and mixtures thereof. The bis(triorganosilyl) dicarboxylate (b1) for the additive has the structure of formula (B-I):



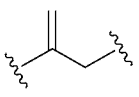
where each R¹ is independently a monovalent hydrocarbon group having from 1 to 12 carbon atoms or a monovalent halogenated hydrocarbon group having from 1 to 12 carbon atoms, and R² is a single carbon-carbon bond or a divalent hydrocarbon group having 1 to 12 carbon atoms.

“Monovalent hydrocarbon group” means a univalent group made up of hydrogen and carbon atoms. Monovalent hydrocarbon group includes alkyl, alkenyl, and aryl groups as defined above. Desirably, each R¹ is independently selected from an alkyl having 1 to 6 carbon groups, an aryl having 6 to 12 carbon groups, or combinations thereof. Suitable alkyl groups for R¹ may include, for example, methyl, ethyl, propyl (e.g., iso-propyl and/or n-propyl), butyl (e.g., isobutyl, n-butyl, tert-butyl, and/or sec-butyl), pentyl (e.g., isopentyl, neopentyl, and/or tert-pentyl), hexyl, as well as branched saturated hydrocarbon groups of 6 carbon atoms. Suitable aryl groups for R¹ may include, for example, cyclopentadienyl, phenyl, anthracenyl, naphthyl, tolyl, xylyl, benzyl, phenylethyl, phenyl propyl, and phenyl butyl. Desirably, each R¹ is independently an alkyl group having 1 to 6 carbon atoms, such as methyl, ethyl, or combinations thereof. More desirably, each R¹ is independently selected from methyl, ethyl, or combinations thereof.

“Monovalent halogenated hydrocarbon group” means a monovalent hydrocarbon group where one or more hydrogen atoms bonded to a carbon atom have been formally replaced with a halogen atom. Halogenated hydrocarbon groups include haloalkyl groups, halogenated carbocyclic groups, and haloalkenyl groups. Haloalkyl groups include fluorinated alkyl groups and fluorinated cycloalkyl groups such as trifluoromethyl (CF₃), fluoromethyl, trifluoroethyl, 2-fluoropropyl, 3,3,3-trifluoropropyl, 4,4,4-trifluorobutyl, 4,4,4,3,3-pentafluorobutyl, 5,5,5,4,4,3,3-heptafluoropentyl, 6,6,6,5,5,4,4,3,3-nonafluorohexyl, 8,8,8,7,7-pentafluorooctyl, 2,2-difluorocyclopropyl, 2,3-difluorocyclobutyl, 3,4-difluorocyclohexyl, and 3,4-difluoro-5-methylcycloheptyl; and chlorinated alkyl and chlorinated cycloalkyl groups such as chloromethyl, 2-chloroethyl, 2-fluoroethyl, 3-chloropropyl, 3,3,3-trifluoropropylsilyl, 2,2-dichlorocyclopropyl, 2,3-dichlorocyclopentyl.

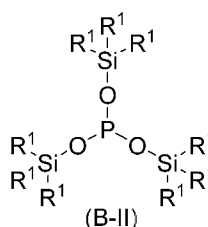
R² may have from 1 to 10 carbon atoms, from 1 to 6 carbon atoms, or from 1 to 3 carbon atoms. Desirably, R² is a divalent aliphatically saturated or unsaturated hydrocarbon group. More desirably, R² is an alkylene group (i.e., divalent aliphatically saturated hydrocarbon group) having from 1 to 10 carbon atoms, from 1 to 6 carbon atoms, or from 1 to 3 carbon atoms. Alternatively, R² is a divalent aliphatic hydrocarbon group having one or more carbon-carbon double bonds and

having 1 to 10 carbon atoms, desirably having 1 to 6 carbon atoms. Examples of suitable R² groups

include -CH₂-, -CH₂CH₂-, -CH₂CH₂CH₂-, -CH=CH-, or .

Suitable bis(triorganosilyl) dicarboxylates may include, for example, bis(trimethylsilyl) malonate, bis(trimethylsilyl) itaconate, bis(trimethylsilyl)oxalate, bis(trimethylsilyl) succinate, bis(trimethylsilyl) glutarate, bis(trimethylsilyl)fumarate, or mixtures thereof. Desirably, the bis(triorganosilyl) dicarboxylates (b1) is selected from the group consisting of bis(trimethylsilyl) malonate, bis(trimethylsilyl) itaconate, and mixtures thereof. More desirably, the bis(triorganosilyl) dicarboxylates (b1) is bis(trimethylsilyl) itaconate.

The tris(triorganosilyl) phosphite (b2) for the additive has the structure of formula (B-II):



where R¹ is as described in formula (B-I) above. Desirably, each R¹ is independently selected from the group consisting of 2-chloroethyl, 2-fluoroethyl, 3,3,3-trifluoropropyl, ethyl, and methyl, more desirably methyl.

Suitable tris(triorganosilyl) phosphites may include, for example, tris(trimethylsilyl) phosphite, tris(triethylsilyl) phosphite, tris(2-chloroethylsilyl) phosphite, tris(2-fluoroethylsilyl) phosphite, tris(3,3,3-trifluoropropylsilyl) phosphite, or mixtures thereof.

The additive (ii) useful in the present invention may comprise, or can consist of, bis(trimethylsilyl) malonate, bis(trimethylsilyl) itaconate, tris(trimethylsilyl) phosphite, or mixtures thereof. Desirably, the additive (ii) is selected from bis(trimethylsilyl) itaconate, tris(trimethylsilyl) phosphite, or mixtures thereof.

The additive (ii) can form the adduct (B) with the alkali metal compound (i) through an acid-base reaction. That is, the adduct (B) is the reaction product of the alkali metal compound (i) with the additive (ii). The adduct can be, for example, a salt (e.g., an alkali metal salt of the additive) or complex resulting from the contact of the additive (ii) with the alkali metal compound (i).

The amount of the adduct (B) in the polyorganosiloxane composition may be in a range of from 0.0003 to 0.03 wt%, and can be 0.0004 wt% or more, 0.005 wt% or more, 0.006 wt% or more, even 0.007 wt% or more while at the same time 0.03 wt% or less, and can be 0.025 wt% or less, 0.020 wt% or less, 0.015 wt% or less, or even 0.01 wt% or less, desirably from 0.0003 to 0.015 wt%, more desirably 0.0007 to 0.01 wt%, based on the weight of the alkenyl-functional

polyorganosiloxane (component (A)).

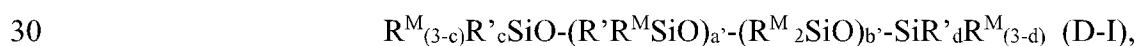
The polyorganosiloxane composition of the present invention may comprise or be free of component (C) one or more cyclic polydiorganosiloxanes of formula (C-I):



5 where R' and R^M are as described above; subscript n is an integer of from 3 to 20, from 3 to 10, or from 3 to 6; and subscript e is 0, 1 or 2.

Suitable cyclic polydiorganosiloxanes (C) may include, for example, cyclic polydimethylsiloxanes such as octamethylcyclotetrasiloxane (D_4), decamethylcyclopentasiloxane (D_5), dodecamethylcyclohexasiloxane (D_6), and other cyclic polydimethylsiloxanes such as D_7 ,
 10 D_8 , D_9 and D_{10} ; cyclic vinylmethylsiloxanes; 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane; tetramethyltetraphenylcyclotetrasiloxane; octaphenylcyclotetrasiloxane; octavinylcyclotetrasiloxane; or mixtures thereof. The cyclic polydiorganosiloxanes typically comprise D_4 , D_5 , D_6 , or mixtures thereof. "D" followed by a number refers to the number of repeating diorganosiloxanes in a cyclic chain. The
 15 polyorganosiloxane composition of the present invention comprises lower amounts of D_4 to D_6 cyclic polydiorganosiloxanes than incumbent polydiorganosiloxane compositions prepared by using bis(trimethylsilyl) vinylphosphonate to neutralize the alkali metal compound catalyst. For example, each of D_4 , D_5 , and D_6 cyclic polydiorganosiloxanes may be present, based on the total weight of the polyorganosiloxane composition, at a concentration less than 0.1 wt%, and can be
 20 less than 0.09 wt%, less than 0.08 wt%, less than 0.07 wt%, less than 0.06 wt%, or even less than 0.05 wt%. Alternatively, the total amount of D_4 , D_5 , and D_6 cyclic polydiorganosiloxanes may be, based on the total weight of the polyorganosiloxane composition, less than 0.3 wt%, and can be less than 0.25 wt%, less than 0.2 wt%, or even less than 0.15 wt%.

The polyorganosiloxane composition of the present invention may comprise or be free of
 25 (D) a low molecular weight alkenyl-terminated polyorganosiloxane (also referred to as "endblocker", component (D)) that has a degree of polymerization between 0 to less than 20, desirably from 3 to 15, more desirably from 5 to 10. The low molecular weight alkenyl-terminated polyorganosiloxane can be linear or branched. The low molecular weight alkenyl-terminated polyorganosiloxane may have the general formula (D-I):

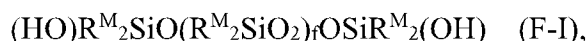


30 where R^M , R' , subscripts c and d are described above in formula (A-I), subscript $a' \geq 0$, subscript $b' \geq 0$, $(a'+b') < 20$, desirably from 3 to 15, more desirably from 5 to 10.

Specified examples of endblockers include $Vi(CH_3)_2SiO[(CH_3)_2SiO]_7Si(CH_3)_2Vi$, where Vi represents vinyl, available from Gelest, Inc., such as DMS-V05.

The polyorganosiloxane composition of the present invention may comprise or be free of component (E) an additional neutralizer, an alkali metal adduct of the additional neutralizer, or mixtures thereof. The additional neutralizer is different from the additive (ii) described above. Suitable additional neutralizers may include, for example, CO₂, an alkylphosphonate, an alkenylphosphonate, an alkylphosphonic acid, a chlorosilane, a phosphate, a phosphoric acid, an inorganic acid, or mixtures thereof. The alkali metal adduct of the additional neutralizer herein refers to the reaction product of the additional neutralizer with the alkali metal compound (i) described above. The concentration of the additional neutralizer may be from zero to 0.05 wt%, from 0.001 to 0.03 wt%, or from 0.001 to 0.002 wt%, based on the total weight of the polyorganosiloxane composition.

The polyorganosiloxane composition of the present invention may comprise or be free of component (F) a hydroxyl-terminated polydiorganosiloxane of unit formula (F-I):



where each R^M is as described above in formula (A-I); and subscript f has a value of from 15 to 50. Desirably, each R^M is independently an alkyl group of 1 to 6 carbon atoms such as methyl.

The hydroxyl-terminated polydiorganosiloxane (F) may comprise one or a combination of two or more polydiorganosiloxane of unit formula (F-I) that may differ in properties such as structure, and sequence. Suitable hydroxyl-terminated polydiorganosiloxanes may comprise any one or any combination of more than one of the following polydiorganosiloxanes: i) bis-hydroxyl-terminated polydimethylsiloxane, ii) bis-hydroxyl-terminated poly(dimethylsiloxane/methylphenylsiloxane), iii) bis-hydroxyl-terminated poly(dimethylsiloxane/diphenylsiloxane), and iv) phenyl,methyl,hydroxyl-siloxy-terminated polydimethylsiloxane. Desirably, the hydroxyl-terminated polydiorganosiloxane comprises bis-hydroxyl-terminated polydimethylsiloxane.

The hydroxyl-terminated polydiorganosiloxane (F) may be present in the polyorganosiloxane composition at a concentration of from zero to 10 wt%, 1 to 8 wt%, or 3 to 5 wt%, based on the total weight of the polyorganosiloxane composition.

The present invention also relates to a method of preparing the polyorganosiloxane composition describe above. The method comprises the steps of: a) contacting a mixture comprising the alkenyl-functional polydiorganosiloxane (A) and the alkali metal compound (i) with the additive (ii), and optionally step b) herein below.

The mixture typically results from the ring opening polymerization of one or more cyclic polydiorganosiloxanes in the presence of the alkali metal compound (i) as a catalyst at elevated temperatures, typically above 100 °C and below 300 °C. The ring opening reaction of cyclic polydiorganosiloxanes for preparing polyorganosiloxanes are known in the art. The cyclic

polydiorganosiloxanes are as described above for component (C). Desirably, the cyclic polydiorganosiloxanes used for the ring opening polymerization include D₄, D₅, D₆, D₇ to D₁₀, or mixtures thereof. The alkali metal compound (i) may be present in the mixture in an amount of from 0.001 to 0.2 wt%, and can be 0.001wt% or more, 0.002 wt% or more, 0.005 wt% or more, 0.01 wt% or more, 0.02 wt% or more, even 0.05 wt% or more while at the same time is 0.2 wt% or less, and can be 0.18 wt% or less, 0.15 wt% or less, 0.12 wt% or less, or even 0.10 wt% or less, desirably, from 0.01 to 0.15 wt%, more desirably, from 0.01 to 0.1 wt%, based on the weight of the alkenyl-functional polyorganosiloxane (A).

The amount of the additive (ii) used in the method can be any amount capable of reacting all or at least a portion of the alkali metal compound (i) present in the polyorganosiloxane mixture through an acid-base reaction, thereby forming the adduct (B) described above with the alkali metal compound. Generally, it is preferred to provide at least a stoichiometric excess of the additive relative to the alkali metal atoms present in the mixture. For example, the additive (ii) may be used in an amount sufficient to provide a molar ratio of trimethylsilyloxy (OTMS) groups in the additive to alkali metal atoms in the alkali metal compound (hereinafter referred to as “OTMS/Alkali metal ratio”) greater than 1.1:1. The OTMS/Alkali metal ratio can be 1.2:1 or higher, 1.3:1 or higher, 1.4:1 or higher, 1.5:1 or higher, 1.8:1 or higher, or even 2.0:1 or higher. The OTMS/Alkali metal ratio can be 4.0:1 or lower, 3.0:1 or lower, 2.5:1 or lower, 2.2:1 or lower, 2.1:1 or lower, or even 2.0:1 or lower. Alternatively, the additive (ii) may be used in an amount of from 0.0005 to 0.05 wt%, and can be 0.00005 wt% or more, 0.0007 wt% or more, 0.008 wt% or more, 0.010 wt% or more, even 0.012 wt% or more while at the same time is 0.05 wt% or less, 0.04 wt% or less, 0.03 wt% or less, or even 0.025 wt% or less, desirably from 0.0007 to 0.03 wt%, more desirably from 0.0008 to 0.025 wt%, based on the weight of the alkenyl-functional polyorganosiloxane (A).

Contacting the mixture with the additive (ii) in step a) of the method may be conducted at room temperature (20-25 °C) or at elevated temperatures, for example, in a range of from 80 to 300 °C, and can be 100 °C or higher, 120 °C or higher, 150 °C or higher, 160 °C or higher, even 170 °C or higher while at the same time is 300 °C or lower, and can be 275 °C or lower, 250 °C or lower, even 225° C or lower.

The method of preparing the polyorganosiloxane composition may optionally also comprise addition of the additional neutralizer (E) described above to the mixture prior to or during contacting the mixture with the additive.

The method of preparing the polyorganosiloxane composition may optionally further comprise step b): stripping the neutralized mixture obtained from step a). Stripping is typically

conducted under vacuum at elevated temperatures to remove cyclic polydiorganosiloxanes from the neutralized mixture. The pressure in the vacuum may range from 1 to 10,000 pascals (Pa) (aka atmospheric pressure), desirably from 1 to 100 Pa. Temperatures for the stripping can be in a range of from 100 to 300 °C, from 150 to 250 °C, or from 170 to 220 °C.

5 The method of preparing the polyorganosiloxane composition can be conducted as a batch process or as a continuous process. The method of preparing the polyorganosiloxane composition may comprise, or be free of, an extra step for separation of the adduct from the resultant polyorganosiloxane composition, e.g., by means of settling or filtration, while still affording the obtained polyorganosiloxane composition with improved thermal stability, or even improved
10 clarity.

 The polyorganosiloxane composition of the present invention or the polyorganosiloxane composition obtained by the method is thermally stable as indicated by reduced amounts of one or more of D₄ to D₆ cyclic polydiorganosiloxanes, and may even show improved (i.e., higher) clarity; particularly when subject to heating at temperatures higher than 120 °C, desirably 150 °C
15 or higher, more desirably 180 °C or higher, as compared to incumbent polyorganosiloxane compositions prepared by involving neutralization of alkali metal compounds (e.g., catalysts) using a conventional neutralizer, i.e., bis(trimethylsilyl) vinylphosphonate. For example, the polyorganosiloxane composition of the present invention, when subject to heating at 180 °C for 1 hour, may also demonstrate improved clarity, as indicated by light transmittance greater than 84%
20 at wavelengths ranging from 450 to 650 nanometers (nm). The above properties can be measured according to the test methods described in the Examples section below. Thus, the method is particularly suitable for preparing the polyorganosiloxane composition with improved clarity.

 The present invention also relates to a process for stabilizing or neutralizing a mixture comprising the alkenyl-functional polyorganosiloxane (A) and the alkali metal compound (i). The
25 process comprises the steps of: contacting the mixture with the additive (ii). When the process is for neutralizing the mixture, the additive (ii) is used in a neutralizing amount. “Neutralizing amount” means that the additive is present at a concentration sufficient to neutralize at least a portion of, desirably all of, the alkali metal compound in the mixture. For example, the amount of the additive used is described in the method of preparing the polyorganosiloxane composition
30 section above, e.g., the OTMS/Alkali metal ratio described above. Conditions for contacting the mixture with the additive (ii) is as described in the method of preparing the polyorganosiloxane composition section above. When the process is for stabilizing the mixture, the additive is used in a stabilizing amount. “Stabilizing amount” means that the additive is present at a concentration sufficient to reduce the amount of one or more of D₄, D₅ and D₆ cyclic polydiorganosiloxanes,

when subject to heating at temperatures higher than 120 °C, desirably 150 °C or higher, more desirably 180 °C or higher, as compared to incumbent polyorganosiloxane compositions prepared by involving neutralization of the alkali metal compounds (e.g., catalysts) with bis(trimethylsilyl) vinylphosphonate.

5

EXAMPLES

Some embodiments of the invention will now be described in the following Examples, wherein all percentages (%) are by weight relative to Vinyl Polymer (component (A) weight), unless otherwise specified. Table A lists the materials for use in the composition of the samples described herein below. Note: “D₄” represents octamethylcyclotetrasiloxane, “D₅” represents decamethylcyclopentasiloxane, and “D₆” represents dodecamethylcyclohexasiloxane. DOWSIL is a trademark of The Dow Chemical Company.

10

Table A

Component		Chemical Description	Source
A	Vinyl Polymer	Vinyl dimethyl terminated polydimethylsiloxane with a viscosity of 450 centistokes (cSt) as measured according to ASTM D 1084 at 25 °C and 0.44 wt% vinyl	Available from The Dow Chemical Company
B Catalyst	Catalyst b-2	Potassium silanolate with an average potassium (K) content of 3.5 % by weight based on Catalyst weight	Synthesized according to US2567110
C Additive	BisTMS malonate	Bis(trimethylsilyl) malonate	Available from Tokyo Chemical Industry Co., Ltd.
	TrisTMS phosphite	Tris(trimethylsilyl) phosphite	Available from Tokyo Chemical Industry Co., Ltd.
	BisTMS itaconate	Bis(trimethylsilyl) itaconate	Available from Gelest
C' Additive	Bis(trimethylsilyl) vinylphosphonate Mixture (“BisTMS VPA Mixture”)	A mixture of trimethylsilyl vinylphosphonic acid, vinylphosphonic acid, and bistrimethylsilyl vinylphosphonic acid	Synthesized according to Example 1 of US5481014
	TMS acetate	Trimethylsilyl acetate	Available from Tokyo Chemical Industry Co., Ltd.
	AcOH	Acetic acid	Available from Sinopharm Chemical Reagent Co., Ltd.
	Propionic acid		Available from Sinopharm Chemical Reagent Co., Ltd.
	Tris(2-chloroethyl) phosphite		Available from Tokyo Chemical Industry Co., Ltd.
	TrisTMS phosphate	Tris(trimethylsilyl) phosphate	Available from Tokyo Chemical Industry Co., Ltd.

Preparation of Masterbatch Solutions

Below catalyst or neutralizer masterbatch solutions were prepared by using a speedy mixer at 800 revolutions per minute (rpm) for 30 seconds to mix the components together.

15

1) Catalyst b-2 masterbatch solution was prepared by mixing 150 grams (g) of Vinyl Polymer with 1.5 g of Catalyst b-2.

2) Each neutralizer masterbatch solution was prepared by mixing 0.1 g of the neutralizer with 10 g of Vinyl Polymer.

5 Inventive Examples (IEs) 1-11 and Comparative Examples (CEs) 1-12

Formulations for inventive and comparative polyorganosiloxane compositions are in Table 1, with the amount of each component reported in parts by weight.

10 Add 10 g of the catalyst masterbatch solution prepared above into each of 40 mL glass scintillation vials equipped with magnetic stir bars, and then add specified amounts of the neutralizer masterbatch solutions prepared above into these vials, based on formulations listed in Table 1, 4, 5 and 6, to form comparative and inventive polyorganosiloxane compositions. The specified amount used for each neutralizer masterbatch solution is given below:

15 150 milligrams (mg) of BisTMS VPA Mixture masterbatch solution, 220 mg of BisTMS malonate masterbatch solution, 250 mg of BisTMS itaconate masterbatch solution, 190 mg of TrisTMS phosphate masterbatch solution, 180 mg of TrisTMS phosphite masterbatch solution, 110 mg of AcOH masterbatch solution, 220 mg of TMS acetate masterbatch solution, 133 mg of propionic acid masterbatch solution, or 161 mg of tris(2-chloroethyl) phosphite masterbatch solution.

20 These vials containing the polyorganosiloxane compositions were flushed with nitrogen and then sealed and placed in an oil bath on a stirring plate with temperature pre-adjusted to 180 °C. The vials were stirred and heated at 180 °C for 1 hour and then cooled down to room temperature to give samples for characterization.

25 The obtained samples (also referred to as “unstripped samples”) were then characterized for the contents of cyclics according to the Gas Chromatography (GC) Measurement and transmittance properties according to the Transmittance Measurement, both described below.

Some of the samples were then subjected to steam stripping (hereinafter referred to as “vacuum stripped samples”) according to the conditions described in the Stripping Process below, prior to the GC measurement.

Stripping Process

30 Vacuum stripped samples were prepared as below:

3 g of the unstripped sample obtained above in the scintillation vials were then transferred into a headspace GC vial (HSGC vial, 10 mL scale) with a rubber septum on the top, and the headspace GC vial was placed in an oil bath. A Schlenk line was used, anti-pressure rubber tube was connected to the Schlenk line, and a syringe and needle was then connected with the tube.

The needle was inserted into the rubber septum on the HSGC vial so that vacuum can be applied to it. The stripping process was conducted at 180 °C for 15 minutes using an oil pump. The obtained vacuum stripped samples were then evaluated for contents of cyclics according to the GC measurement described above.

5 Gas Chromatography Measurement

Gas chromatography (GC) was used to measure cyclics level for all the samples. A sample (0.2 gram (g)) was weighed into a 12 millimeter (mL) glass vial, and then treated with 5 mL of acetone, 4 microliter (μL) of dodecane was used as an internal standard. The mixture was shaken for 1 hour on a shaker. The obtained acetone solution was analyzed using gas chromatography with flame ionization detection after centrifugation. Experimental relatively response factor (RRF: 2.27) was employed for calculation.

The GC instrument conditions and parameters used are as below:

GC Instrument: Agilent 7890N

Oven: 40°C (5 min) at 15°C/min - 320°C (0 min).

15 Inlet: 300°C, 18.5 psi, splitless.

Column: DB-5 MS UI, 30 m×0.25 mm×0.25 μm.

Detector: FID, Temperature: 320°C, H₂ flow: 30.0 mL/min, Air flow: 400.0 mL/min, Makeup flow: 25 mL/min.

Injection volume: 1.0 μL.

20 Transmittance Measurement

Transmittance properties of samples were measured using a SHIMADZU's UV-1900 UV-vis spectrophotometer. The samples prepared above was directly added into the cuvette for measurement. The transmittance properties of the samples (i.e., polyorganosiloxane compositions comprising alkali metal salts of an additive in Vinyl Polymer) were measured.

25 Characterization results of cyclic generation (such as D₄, D₅ and D₆) in the samples are given in Tables 1-6. Samples are unstripped samples, unless otherwise specified. If the concentration of any one of D₄, D₅, and D₆ is reduced by at least 5 ppm, or the total concentration of D₄, D₅, and D₆ is reduced by 10 ppm or more, it means significant difference.

Table 1

<i>Component</i>	CEs 1, 2, 3, and 5	IEs 1 and 2	IEs 3 and 5	CEs 4 and 6	IEs 4 and 6
Vinyl Polymer	100	100	100	100	100
Potassium silanolate	0.1	0.1	0.1	0.1	0.1
BisTMS VPA Mixture	0.015				
BisTMS malonate		0.022			
BisTMS itaconate			0.025		

TrisTMS phosphate				0.019	
TrisTMS phosphite					0.018
Characterization					
K/Reactive acidic groups Ratio	0.5	0.5	0.5	0.5	0.5

In Tables 1 and 4-7:

“K/Reactive acidic groups Ratio” refers to the molar ratio of potassium (K) in the catalyst to the total acidic groups (i.e., trimethylsilyloxy (OTMS) and hydroxy (OH) groups if present) in the neutralizer.

5 Table 2 shows comparison of cyclic generation for polyorganosiloxane compositions using different neutralizers after heating at 180 °C for 1 hour, before and after stripping. IE 1 sample using BisTMS malonate showed less cyclics than CE 1 using BisTMS VPA Mixture. The sample using BisTMS malonate after vacuum stripping (IE 2) still showed less cyclics than the vacuum stripped sample using BisTMS VPA Mixture (CE 2).

Table 2

Sample		CE 1	IE 1	CE 2 (vacuum stripped)	IE 2 (vacuum stripped)
Cyclic concentration	D ₄ (wt%)	0.0589	0.0552	0.0312	0.0126
	D ₅ (wt%)	0.0579	0.0566	0.0364	0.021
	D ₆ (wt%)	0.0332	0.033	0.0237	0.0188
	D ₄ -D ₆ (wt%)	0.15	0.1448	0.0914	0.0524

In Tables 2-6:

The weight concentration of D₄ (octamethylcyclotetrasiloxane), D₅ (decamethylcyclopentasiloxane), and D₆ (dodecamethylcyclohexasiloxane), respectively, is relative to the composition sample weight.

The concentration of D₄-D₆ is weight concentration of total amounts of D₄, D₅, and D₆ relative to the composition sample weight.

Table 3 gives characterization results of cyclic generation for samples using different neutralizers, before and after stripping. It shows that the cyclic levels of samples with BisTMS itaconate (IE 3) and TrisTMS phosphite (IE 4) were lower than those using BisTMS VPA Mixture (CE 3) and TrisTMS phosphate (CE 4). After stripping, the cyclic levels of IE 5 (using BisTMS itaconate) and IE 6 (using TrisTMS phosphite) vacuum stripped samples were still lower than CEs 5 and 6 samples (using BisTMS VPA Mixture and TrisTMS phosphate, respectively) vacuum stripped samples.

Table 3

<i>Sample</i>		CE 3	IE 3	CE 4	IE 4	CE 5 (vacuum stripped)	IE 5 (vacuum stripped)	CE 6 (vacuum stripped)	IE 6 (vacuum stripped)
Cyclic concentration	D ₄ (wt%)	0.0593	0.0544	0.0554	0.0549	0.0476	0.0458	0.0461	0.0454
	D ₅ (wt%)	0.058	0.0546	0.0552	0.0545	0.0506	0.0497	0.0486	0.048
	D ₆ (wt%)	0.0367	0.0302	0.0314	0.0312	0.032	0.0293	0.0279	0.0279
	D ₄ -D ₆ (wt%)	0.1539	0.1391	0.142	0.1407	0.1301	0.1249	0.1226	0.1212

Table 4 gives formulations, with the amount of each component reported in parts by weight,

and cyclic levels for samples using different neutralizers such as BisTMS itaconate as compared to TMS acetate (a monocarboxylate) and AcOH (a monocarboxylic acid). As shown in Table 4, IE 7 using BisTMS itaconate provided lower amounts of cyclics than CEs 7 and 8 using acetic acid and TMS acetate.

5

Table 4

Component	CE 7	CE 8	IE 7
Vinyl Polymer	100	100	100
Catalyst b-2 Potassium silanolate	0.1	0.1	0.1
AcOH	0.011		
TMS acetate		0.024	
BisTMS itaconate			0.025
Characterization			
K/Reactive acidic groups Ratio	0.5	0.5	0.5
D ₄ (wt%)	0.0441	0.0442	0.0433
D ₅ (wt%)	0.0351	0.0348	0.0346
D ₆ (wt%)	0.0173	0.0166	0.0166
D ₄ -D ₆ (wt%)	0.0964	0.0957	0.0944

Table 5 gives formulations, with the amount of each component reported in parts by weight, and cyclic levels for samples using BisTMS itaconate comparing with propionic acid as neutralizers. The cyclic levels for IE 8 were lower than that of CE 9.

10

Table 5

Components	CE 9	IE 8
Vinyl Polymer	100	100
Catalyst b-2 Potassium silanolate	0.1	0.1
Propionic acid	0.0133	
BisTMS itaconate		0.025
Characterization		
K/Reactive acidic groups Ratio	0.5	0.5
D ₄ (wt%)	0.0433	0.0429
D ₅ (wt%)	0.0356	0.0355
D ₆ (wt%)	0.0217	0.0183
D ₄ -D ₆ (wt%)	0.1006	0.0967

Table 6 gives formulations, with the amount of each component reported in parts by weight, and cyclic levels for samples using different types of phosphites as neutralizes. The use of TrisTMS phosphite for IE 9 gave lower contents of each of D₄, D₅, and D₆, and the combined content of D₄ to D₆ than the use of Tris(2-chloroethyl) phosphite for CE 10.

15

Table 6

Component	CE 10	IE 9
Vinyl Polymer	100	100
Catalyst b-2 Potassium silanolate	0.1	0.1
Tris(2-chloroethyl) phosphite	0.0161	
TrisTMS phosphite		0.0179
Characterization		

K/Reactive acidic groups Ratio	0.5	0.5
D ₄ (wt%)	0.0592	0.0575
D ₅ (wt%)	0.0484	0.0476
D ₆ (wt%)	0.0252	0.0236
D ₄ -D ₆ (wt%)	0.1328	0.1287

In summary, the inventive polyorganosiloxane compositions obtained by treating the base catalyst with the specific neutralizers (e.g., BisTMS malonate, BisTMS itaconate, and TrisTMS phosphite) have demonstrated lower level of individual cyclic D₄, D₅, and/or D₆ as well as overall amounts of D₄-D₆ cyclics, both before and after vacuum stripping, as compared to the specified CE samples using different neutralizers. It indicates that IE samples were more thermally stable (i.e., less depolymerization after treating the catalyst with the neutralizers).

Some samples (CEs 11 and 12, IEs 10 and 11) were characterized for transmittance properties. Table 7 gives formulations, with the amount of each component reported in parts by weight, and transmittance properties of these samples. As shown in Table 7, IEs 10 and 11 using BisTMS malonate and TrisTMS phosphite as neutralizers, respectively, provided the obtained samples with higher transmittance, as compared to CEs 11 and 12 using comparative neutralizers such as BisTMS VPA Mixture and TrisTMS phosphate. As compared to CEs 11 and 12 samples, IEs 10 and 11 samples both showed higher light transmittance from 450 to 650 nm wavelength (all achieving 85% or higher transmittance), indicating higher clarity and better appearance.

Table 7

Component	CE 11	CE 12	IE 10	IE 11
Vinyl Polymer	100	100	100	100
Catalyst b-2 Potassium silanolate	0.1	0.1	0.1	0.1
BisTMS VPA Mixture	0.015			
TrisTMS phosphate		0.019		
BisTMS malonate			0.022	
TrisTMS phosphite				0.018
Characterization				
K/Reactive acidic groups Ratio	0.5	0.5	0.5	0.5
450 nm (% transmittance)	77.477	80.928	85.605	89.099
550 nm (% transmittance)	81.313	84.557	87.906	90.61
650 nm (% transmittance)	83.958	87.019	89.392	91.548

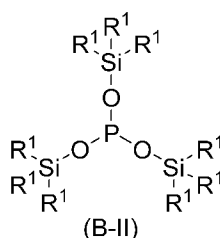
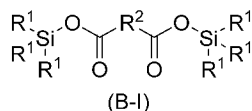
CLAIMS:

1. A polyorganosiloxane composition, comprising:

(A) an alkenyl-functional polyorganosiloxane having an average of at least two alkenyl groups per molecule; and

5 (B) an adduct of (i) an alkali metal compound with (ii) an additive,

wherein the additive (ii) is selected from the group consisting of (b1) a bis(triorganosilyl) dicarboxylate of formula (B-I), (b2) a tris(triorganosilyl) phosphite of formula (B-II), and mixtures thereof;



where each R^1 is independently a monovalent hydrocarbon group having from 1 to 12 carbon atoms or a monovalent halogenated hydrocarbon group having from 1 to 12 carbon atoms; and R^2 is a single carbon-carbon bond or a divalent hydrocarbon group having 1 to 12 carbon atoms.

2. The composition of claim 1, where, in formula (B-I), R^2 is an alkylene group having 1 to 10 carbon atoms.

3. The composition of claim 1, where, in formula (B-I), R^2 is a divalent aliphatic hydrocarbon group having a carbon-carbon double bond and 1 to 10 carbon atoms.

4. The composition of any one of claims 1-3, where, in formula (B-I) and (B-II), R^1 is methyl.

5. The composition of claim 1, wherein the bis(triorganosilyl) dicarboxylate (b1) is selected from the group consisting of bis(trimethylsilyl) malonate, bis(trimethylsilyl) itaconate, bis(trimethylsilyl)oxalate, bis(trimethylsilyl) succinate, bis(trimethylsilyl) glutarate, bis(trimethylsilyl)fumarate, and mixtures thereof.

6. The composition of claim 1, wherein the tris(triorganosilyl) phosphite (b2) is selected from the group consisting of tris(trimethylsilyl) phosphite, tris(triethylsilyl) phosphite, tris(2-chloroethylsilyl) phosphite, tris(2-fluoroethylsilyl) phosphite, tris(3,3,3-trifluoropropylsilyl) phosphite, and mixtures thereof.

7. The composition of any one of claims 1-6, wherein the alkenyl-functional polyorganosiloxane has an average chemical structure:



where each R^M is independently an alkyl group having 1 to 6 carbon atoms or an aryl group having 6 to 12 carbon atoms, each R' is independently an alkenyl group having 2 to 12 carbon atoms, subscript $a \geq 0$, subscript $b \geq 0$, subscript c is 0 or 1, subscript d is 0 or 1, $(a+b)$ is in a range of from 20 to 10000, and $(a+c+d) \geq 2$.

8. The composition of any one of claims 1-7, wherein the alkenyl-functional polyorganosiloxane is selected from the group consisting of i) dimethylvinylsiloxo-terminated polydimethylsiloxane, ii) dimethylvinylsiloxo-terminated poly(dimethylsiloxane/methylvinylsiloxane), iii) dimethylvinylsiloxo-terminated polymethylvinylsiloxane, iv) trimethylsiloxo-terminated poly(dimethylsiloxane/methylvinylsiloxane), v) trimethylsiloxo-terminated polymethylvinylsiloxane, vi) dimethylvinylsiloxo-terminated poly(dimethylsiloxane/methylvinylsiloxane), vii) dimethylvinylsiloxo-terminated poly(dimethylsiloxane/methylphenylsiloxane), viii) dimethylvinylsiloxo-terminated poly(dimethylsiloxane/diphenylsiloxane), viiii) phenyl,methyl,vinyl-siloxo-terminated polydimethylsiloxane, x) dimethylhexenylsiloxo-terminated polydimethylsiloxane, and mixtures thereof.

9. The composition of any one of claims 1-8, wherein the alkali metal compound is selected from the group consisting of a potassium hydroxide, a potassium silanolate, and mixtures thereof.

10. A method of preparing the polyorganosiloxane composition of any one of claims 1-9, comprising the steps of:

- a) contacting a mixture comprising the alkenyl-functional polyorganosiloxane (A) and the alkali metal compound (i) with the additive (ii), and optionally,
- b) stripping the neutralized mixture obtained from step a).

11. The method of claim 10, wherein the step a) is conducted at temperatures ranging from 80 to 300 °C.

INTERNATIONAL SEARCH REPORT

International application No

PCT/CN2023/140549

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08K5/11 C08K5/5415 C08L83/04
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 C08K 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	WO 2010/009754 A1 (MOMENTIVE PERFORMANCE MAT INC [DE]; STEINBERGER HELMUT [DE] ET AL.) 28 January 2010 (2010-01-28)	1,4,6-8, 10,11
A	page 3, line 1 - page 6, line 7 page 25, line 4 - page 26, line 4 examples 3, 5	2,3,5,9
A	----- US 8 426 506 B2 (MUELLER JOHANN [DE]; MERGET MARKUS [DE] ET AL.) 23 April 2013 (2013-04-23) column 1, line 42 - line 54 column 5, line 21 - line 47 -----	1-11
A	US 7 736 634 B2 (SIGMA COATINGS BV [NL]) 15 June 2010 (2010-06-15) column 3, line 41 - line 67 column 5, line 11 - line 19 -----	1-11



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

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