ORGANOPOLYSILOXANES FOR COMPATABILIZING POLYHETEROSILOXANES

An organosiloxane is disclosed having the formula: \((R^1)_{2n+1}SiO_{n+2}\) where \(n\) is 1 or 2, \(R^1\) is independently a monovalent \(C_1\) to \(C_{10}\) hydrocarbyl, \(R^2\) is a divalent \(C_2\) to \(C_{10}\) hydrocarbyl, \(R^3\) is independently a monovalent \(C_1\) to \(C_{10}\) hydrocarbyl containing at least one aryl group, \(X\) is a hydrolyzable group selected from \(-OR^4, Cl, -OC(0)R^5, -N(R^6)_2\) or \(-ON=CR^7\), where \(R^4\) is hydrogen or a \(C_1\) to \(C_3\) alkyl group.

Declaration under Rule 4.17:
— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(1))
— as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(ii))
— of inventorship (Rule 4.17(iv))

Published:
— with international search report (Art. 21(3))
MONOFUNCTIONAL ORGANOPOLYSILOXANES
FOR
COMPATABILIZING POLYHETEROSILOXANES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of US Application No. 61/661,828 as filed on 20 June, 2012.

BACKGROUND OF THE INVENTION

[0002] Incorporation of various metal elements into polisiloxanes to form polyheterosiloxanes has been of great interest for a wide range of applications due to their ability to impart high refractive index, impact resistance, scratch resistance, fire retardance, anti-corrosion, anti-stain, etc. Methods for preparing polyheterosiloxane materials having at least two different non-Si metal elements has recently been disclosed in WO2011/002826. While the teachings of WO2011/002826 provide polyheterosiloxane compositions that have solubility in various organic solvents, there still remains a need to identify compositions and methods for improving the compatibility of polyheterosiloxane compositions with other polymers, and in particular with polydiorganosiloxanes.

BRIEF SUMMARY

[0003] The present inventors have discovered certain organosiloxane compositions that are useful to enhance the compatibility of polyheterosiloxanes with polydiorganosiloxanes.
The present disclosure relates to an organosiloxane having the formula:

\[(R^1)_3SiO_n(R^1)_{(3-n)}Si-R^2Si(R^1)_2OSi(R^3)_2X\]

where \(n\) is 1 or 2,

- \(R^1\) is independently a monovalent \(C_i\) to \(C_{20}\) hydrocarbyl,
- \(R^2\) is a divalent \(C_2\) to \(C_{12}\) hydrocarbyl,
- \(R^3\) is independently a monovalent \(C_i\) to \(C_{30}\) hydrocarbyl containing at least one aryl group,
- \(X\) is a hydrolyzable group selected from -OR, Cl, -OC(0)R, -N(R)\(_2\), or -ON=CR\(_2\)

where \(R\) is hydrogen or a \(C_i\) to \(C_6\) alkyl group.

The present disclosure further provides a process for preparing an organosiloxane by:

I) reacting:

a) an organosilane of the formula \((R^3)_2Si(OR)\_2\)

where \(R^3\) is independently a monovalent \(C_i\) to \(C_{30}\) hydrocarbyl containing at least one aryl group,

- \(R^4\) is hydrogen or a \(C_i\) to \(C_6\) alkyl group,

b) a disiloxane of the formula \(R^5(R^1)_2SiOSi(R^1)_2R^5\)

where \(R^1\) is independently a monovalent \(C_i\) to \(C_{20}\) hydrocarbyl,

- \(R^5\) is a \(C_2\) to \(C_{12}\) hydrocarbyl having a terminal unsaturated group,

- to form a mixture containing an organosiloxane of the formula \(R^4R^5SiOSi(R^3)_2OR\_4\),

II) optionally, processing the mixture to remove unreacted starting components or other volatile components,

III) reacting the \(R^5(R^1)_2SiOSi(R^3)_2OR\_4\) organosiloxane with

a) an organohydrogensiloxane of the formula \((R^1)_{3}SiO_n(R^1)_{(3-n)}SiH\)

where \(R^1\) is independently a monovalent \(C_i\) to \(C_{20}\) hydrocarbyl,

- \(n\) is 1 or 2, alternatively \(n = 2\), and

b) a hydro silylation catalyst,

IV) optionally, further processing the reaction mixture of step III to remove any volatile components.
DETAILED DESCRIPTION OF THE INVENTION

[0006] The present disclosure relates to an organosiloxane having the formula;  

\[(R^1_3SiO)_n(R^1_3Si-R^2Si(R^1_2OSi(R^3_2))X\]

where \(n\) is 1 or 2,  
\(R^1\) is independently a monovalent C\(_1\) to C\(_{20}\) hydrocarbyl,  
\(R^2\) is a divalent C\(_2\) to C\(_{12}\) hydrocarbyl,  
\(R^3\) is independently a monovalent C\(_{30}\) hydrocarbyl containing at least one aryl group,  
\(X\) is a hydrolyzable group selected from  
- \(-OR^4, CI, -OC(\theta)R^4, -N(R^4)_2\), or \(-ON=CR^4_2\)

where \(R^4\) is hydrogen or a Ci to C\(_6\) alkyl group.

[0007] In the above organosiloxane formula \(R^1\) is independently a monovalent C\(_1\) to C\(_{20}\) hydrocarbyl. The hydrocarbon group may independently be an alkyl, aryl, or alkylaryl group. As used herein, hydrocarbyl also includes halogen substituted hydrocarbysls. \(R^1\) may be a C\(_1\) to C\(_{20}\) alkyl group, alternatively \(R^1\) may be a C\(_1\) to C\(_{18}\) alkyl group. Alternatively \(R^1\) may be a C\(_1\) to C\(_6\) alkyl group such as methyl, ethyl, propyl, butyl, penty, or hexyl. \(R^1\) may be an aryl group, such as phenyl, naphthyl, or an anthryl group. Alternatively, \(R^1\) may be any combination of the aforementioned alkyl or aryl groups. Alternatively, \(R^1\) is phenyl, methyl, or a combination of both. Alternatively \(R^1\) is methyl.

[0008] In the above organosiloxane formula \(R^2\) is divalent hydrocarbon group containing 2 to 12 carbon atoms, alternatively \(R^2\) contains 2 to 6 carbon atoms, alternatively \(R^2\) is ethylene, propylene, or isobutylene, alternatively \(R^2\) is ethylene (\(-CH_2CH_2\)).

[0009] \(R^3\) is independently a monovalent C\(_1\) to C\(_{30}\) hydrocarbyl containing at least one aryl group. \(R^3\) may be an aryl group, such as phenyl, naphthyl, or an anthryl group. Alternatively, \(R^3\) may be any combination of the aforementioned alkyl or aryl groups.

Alternatively, \(R^3\) is phenyl (C\(_6\)H\(_5\)).

[0010] \(X\) is a hydrolyzable group selected from \(-OR^4\), CI, \(-OC(\theta)R^4\), \(-N(R^4)_2\), or \(-ON=CR^4_2\)

where \(R^4\) is hydrogen or a C\(_1\) to C\(_6\) alkyl group such as a methyl, ethyl, propyl, isopropyl, butyl, penty, or hexyl group. Alternatively, \(R^4\) is methyl. Thus \(X\) may be an alkoxy,
hydroxyl, carboxy, amine, chloride, or oxime group. Alternatively X is -OCH₃, -OCH₂CH₃, -OH, -Cl, or -OC(=0)CH₃. Alternatively X is -OCH₃.

[0011] In one embodiment, the organosiloxane has the following formula;

\[(\text{Me}_3\text{SiO})_2(\text{Me})\text{SiCH}_2\text{CH}_2\text{Si(CH}_3)\text{2OSi(C}_6\text{H}_3)\text{2(OMe)}\]

where Me is a methyl group.

[0012] In an alternative embodiment, the organosiloxane has the formula

\[(\text{R}_1\text{3SiO})_n(\text{R}_1\text{)}(3-n)\text{Si-}\text{G-Si(R}_1\text{)}\text{2OSi(R}_3\text{)}\text{2X}\]

where n is 1 or 2,

\[\text{R}_1\text{ is independently a monovalent C to C}_2\text{0 hydrocarbyl,}\]

\[\text{G is a siloxane or polysiloxane bridging group comprising at least one siloxy unit selected from a (R}_2\text{SiO)}\text{2/2), (RSiO)}\text{2/2), or (SiO4/2) siloxy units, where R may be any organic group,}\]

\[\text{R}_3\text{ is independently a monovalent C to C}_2\text{0 hydrocarbyl containing at least one aryl group,}\]

\[\text{X is a hydrolyzable group selected from -OR)}\text{4, Cl, -OC(0)R)}\text{4, -N(R)}\text{4, or -ON=CR)}\text{4, where R)}\text{4 is hydrogen or a C to C}_6\text{ alkyl group.}\]

[0013] G is a siloxane or polysiloxane bridging group comprising at least one siloxy unit selected from a (R}_2\text{SiO)}\text{2/2), (RSiO)}\text{2/2), or (SiO4/2) siloxy units, where R may be any organic group. G may also be a combination of hydrocarbyl bridging groups, such as the divalent C to C₁₂ hydrocarbyl groups described above for R, and a siloxane or polysiloxane.

[0014] Typically, G is a poly(dimethylsiloxane) of the formula -O(Me)}\text{2SiO)}\text{2/2)}\text{q} where the subscript q may vary from 1 to 20, alternatively from 1 to 10, or alternatively from 1 to 5.

[0015] When the polysiloxane bridging group contains a (RSiO)}\text{3/2), or (SiO)}\text{4/2) siloxy unit(s), it may further contain additional R SiOi)}\text{2) siloxy units to provide endcapping groups. Alternatively, some of the (RSiO)}\text{3/2), or (SiO)}\text{4/2) siloxy unit(s) when present in the bridging group may be silanol terminated.}

[0016] The present organosiloxanes may be prepared by any known methods, or alternatively are prepared according to the methods as described below.
[0017] This disclosure further provides a method for preparing the present organosiloxanes by

I) reacting;
   a) an organosilane of the formula \((R^3)_2\text{Si(OR}^4)\_2\)
      where \(R^3\) is independently a monovalent \(C_1\) to \(C_{30}\) hydrocarbyl containing at least one aryl group,
      \(R^4\) is hydrogen or a \(C_1\) to \(C_6\) alkyl group,
   b) a disiloxane of the formula \(R^5(R^1)_2\text{SiOSi(R}^1)\_2R^5\)
      where \(R^1\) is independently a monovalent \(C_1\) to \(C_2\) hydrocarbyl,
      \(R^5\) is a \(C_2\) to \(C_{12}\) hydrocarbyl having a terminal unsaturated group,
      to form a mixture containing an organosiloxane of the formula
      \(R^\_aR^\_a\text{SiOSi(R}^1)\_2\text{OR}^4\),

II) optionally, processing the mixture to remove unreacted starting components or other volatile components,

III) reacting the \(R^5(R^1)\_2\text{SiOSi(R}^3)\_2\text{OR}^4\) organosiloxane with
   c) an organohydrogensilosiloxane of the formula \((R^1)\_3\text{SiO} \text{n(R}^1)\_n\text{SiH}\)
      where \(R^1\) is independently a monovalent \(C_1\) to \(C_2\) hydrocarbyl,
      \(n\) is 1 or 2, alternatively \(n = 2\), and
   d) a hydrosilylation catalyst,

IV) optionally, further processing the reaction mixture of step III to remove any volatile components.

[0018] The first step involves reacting;
   a) an organosilane of the formula \((R^3)_2\text{Si(OR}^4)\_2\) and
   b) a disiloxane of the formula \(R^5(R^1)\_2\text{SiOSi(R}^1)\_2R^5\)
   to form a mixture containing an organosiloxane of the formula \(R^5(R^1)\_2\text{SiOSi(R}^3)\_2\text{OR}^4\).

[0019] \(R^3\) and \(R^4\) in the \((R^3)_2\text{Si(OR}^4)\_2\) organosilane formula are the same as defined above.

[0020] \(R^1\) in the disiloxane formula \(R^5(R^1)\_2\text{SiOSi(R}^1)\_2R^5\) is the same as defined above. \(R^5\) is this formula is a \(C_2\) to \(C_{12}\) hydrocarbyl having a terminal unsaturated group. The terminal unsaturated group may be either an alkene or alkyne. Typically the terminal unsaturated group is vinyl. \(R^3\) is exemplified by hydrocarbyl groups of the formula \(H_2C=CH^-\), \(H_2C=CHCH_2^-\), \(H_2C=C(CH_3)CH_2^-\), \(H_2C=CHC(CH_3)H^-\), \(H_2C=CHC(CH_3)_2^-\),
H₂C=CHCH₂CH₂⁻, H₂C=CHCH₂CH₃CH₂⁻, and H₂C=CHCH₂CH₂CH₂CH₂⁻. Alternatively, R⁵ is a vinyl group, H₂C=CH⁻.

[0021] The reaction effectuated in step I may be considered as an "equilibration" reaction. As such, the reaction of step I may be conducted under those conditions known in the art for performing organosiloxane equilibration reactions. Typically, a sufficient quantity of an equilibration catalyst is added to enhance the reaction. Suitable, non-limiting, equilibration catalysts include strong acids such as trifluoromethane sulfonic acid.

[0022] The amount of components a) and b) may vary and is not limiting. Typically, the reaction is conducted such that the amount of the disiloxane component b) added in step I) provides a slight molar excess vs the amount of the organosilane component a).

[0023] Representative non-limiting example of organosilanes suitable as component a) in the present process include; dimethoxydiphenylsilane, diethoxydiphenylsilane, phenylmethylmethoxysilane, phenylmethyldiethoxysilane, dimethylmethoxysilane, diethyldimethoxysilane, dimethyldiethoxysilane, phenylmethylmethyisopropoxysilane, diphenylmethyisoproxyisilane, etc.

[0024] Representative non-limiting example of diorganosiloxanes suitable as component b) in the present process include; divinyltetramethyldisiloxane, diallyltetramethyldisiloxane, dihexenyltetramethyldisiloxane, hexamethyldisiloxane, tetramethyldisiloxane, etc.

[0025] The R⁵(R¹)₂SiOSi(R³)₂OR³ organosiloxane of step I) may be prepared by alternative methods. Representative general reactions schemes to prepare the organosiloxane of step I) are summarized below:

a) 2Ph₂Si(OH)₂ + (ViMe₂Si)₂NH + trace acid catalyst → 2ViMe₂SiOSiPh₂(OH) + NH₃
b) Ph₂SiCl₂ + ViMe₂SiOH + acid acceptor → ViMe₂SiOSiPh₂Cl (reference US5364896)
c) 3 Ph₂Si(OH)₂ + PO fluid + ViMe₂SiCl → ViMe₂SiOSiPh₂(OH) + NH₄Cl

d) Ph₂ViSiX (X=Cl or OEt)
e) Ph₂Si(OH)₂ + (HMe₂Si)₂NH + HMe₂SiCl → HMe₂SiOPh₂SiOH
f) Ph₂Si(OH)₂ + (HMe₂Si)₂NH + trace acid catalyst → HMe₂SiOPh₂SiOH
g) Ph₂SiCl₂ + ROH → Ph₂SiCl(OR) + ViMe₂SiOH + acid acceptor → ViMe₂SiOSiPh₂(OR)
h) \( \text{Ph}_2\text{SiCl}_2 + \text{Ac}_2\text{O} \rightarrow \text{Ph}_2\text{SiCl(OAc)} \) (strip off AcCl byproduct) + ViMe\textsubscript{2}SiOH + acid acceptor \( \rightarrow \text{ViMe}_2\text{SiOSiPh}_2(\text{OAc}) \)

i) \( \text{Ph}_2\text{SiCl}_2 + \text{NaOAc} \rightarrow \text{Ph}_2\text{SiCl(OAc)} \) (filter off NaCl byproduct)\(^\wedge \) ViMe\textsubscript{2}SiOH + acid acceptor \( \rightarrow \text{ViMe}_2\text{SiOSiPh}_2(\text{OAc}) \)

j) \( \text{Ph}_2\text{SiOAc}_2 + \text{ViMe}_2\text{SiOH} + \text{acid acceptor} \rightarrow \text{ViMe}_2\text{SiOSiPh}_2(\text{OAc}) \)

k) \( \text{Ph}_2\text{SiX}_2 + (\text{ViMe}_2\text{Si})_2\text{O} + \text{acid} \) (Lewis or protic) \( \rightarrow \text{ViMe}_2\text{SiOSiPh}_2\text{X} + \text{ViMe}_2\text{SiX} \);

X=Cl, OR, OAc,

m) \( \text{ViMe}_2\text{SiOLi} + x \text{D}_3 \rightarrow \text{ViMe}_2\text{SiO(Me}_2\text{SiO)}_3\text{Li} + \text{Ph}_2\text{SiX}_2 \rightarrow \text{ViMe}_2\text{SiO(Me}_2\text{SiO)}_3\text{Ph}_2\text{SiX} + \text{LiX} \) where \( X=\text{Cl} \) (preferred), OAc

n) \( \text{ViMe}_2\text{SiOLi} + x \text{D}_3 \rightarrow \text{ViMe}_2\text{SiO(Me}_2\text{SiO)}_3\text{Li} + \text{acid} \rightarrow \text{ViMe}_2\text{SiO(Me}_2\text{SiO)}_3\text{H} + \text{acid} \) \( \rightarrow \text{ViMe}_2\text{SiO(Me}_2\text{SiO)}_3\text{Ph}_2\text{SiX} \) where \( X=\text{OR} \), amide, N

o) \( \text{HPh}_2\text{SiX} + \text{H}_2\text{C=CHRCH=CH}_2 \rightarrow \text{ViRCH}_2\text{CH}_2\text{Ph}_2\text{SiX} \)

[0026] For \( \text{ViMe}_2\text{SiOSiPh}_2\text{X} \) types, different SiH functional siloxanes may be used, e.g.

\( \text{ViMe}_2\text{SiOSiPh}_2\text{X} + \text{HSi(OSiMe)}_3 \) + Pt cat \( \rightarrow \) (Me\textsubscript{2}SiO\textsubscript{3})\textsubscript{3}SiCH\textsubscript{2}CH\textsubscript{2}Ph\textsubscript{2}SiX alt. use

HMeSi(OSiMe\textsubscript{3})\textsubscript{2}, HMe\textsubscript{2}SiOSiMe\textsubscript{3}, HMe\textsubscript{2}Si(OMe\textsubscript{2}Si)\textsubscript{x}OSiMe\textsubscript{3} (Gelest or make from

Me\textsubscript{2}SiOLi + x \text{D}_3 \rightarrow Me\textsubscript{3}SiO(Me\textsubscript{2}SiO)\textsubscript{3x}Li + Me\textsubscript{2}HSiCl \rightarrow Me\textsubscript{3}SiO(Me\textsubscript{2}SiO)\textsubscript{3x}SiMe\textsubscript{2}H or another alt. Me\textsubscript{3}SiO(Me\textsubscript{2}SiO)\textsubscript{3x}Li + acid \( \rightarrow \) Me\textsubscript{3}SiO(Me\textsubscript{2}SiO)\textsubscript{3x}H + (HMe\textsubscript{2}Si)\textsubscript{2}NH \( \rightarrow \) Me\textsubscript{3}SiO(Me\textsubscript{2}SiO)\textsubscript{3x}SiMe\textsubscript{2}H.

[0027] For HMe\textsubscript{2}SiOSiPh\textsubscript{2}X types, then use different SiVi functional siloxanes, e.g.

HMe\textsubscript{2}SiOSiPh\textsubscript{2}X + ViSi(OSiMe\textsubscript{3})\textsubscript{3} + Pt cat \( \rightarrow \) (Me\textsubscript{2}SiO\textsubscript{3})\textsubscript{3}SiCH\textsubscript{2}CH\textsubscript{2}Ph\textsubscript{2}SiX alt. use

ViMeSi(OSiMe\textsubscript{3})\textsubscript{2}, ViMe\textsubscript{2}SiOSiMe\textsubscript{3} (Gelest), ViMe\textsubscript{2}Si(OMe\textsubscript{2}Si)\textsubscript{x}OSiMe\textsubscript{3} (Gelest or make from

ViMe\textsubscript{2}SiOLi + x \text{D}_3 \rightarrow ViMe\textsubscript{2}SiO(Me\textsubscript{2}SiO)\textsubscript{3x}Li + Me\textsubscript{2}SiCl \( \rightarrow \)

Me\textsubscript{3}SiO(Me\textsubscript{2}SiO)\textsubscript{3x}SiMe\textsubscript{3} or another alt. Me\textsubscript{3}SiOLi + x \text{D}_3 \rightarrow Me\textsubscript{3}SiO(Me\textsubscript{2}SiO)\textsubscript{3x}Li + acid \( \rightarrow \) Me\textsubscript{3}SiO(Me\textsubscript{2}SiO)\textsubscript{3x}H + (ViMe\textsubscript{2}Si)\textsubscript{2}NH \( \rightarrow \) Me\textsubscript{3}SiO(Me\textsubscript{2}SiO)\textsubscript{3x}SiMe\textsubscript{2}Vi.

[0028] Alternatively, direct routes may be used to prepare an organosiloxane intermediate which do not require hydrosilation, e.g. Me\textsubscript{3}SiOLi + x \text{D}_3 \rightarrow Me\textsubscript{3}SiO(Me\textsubscript{2}SiO)\textsubscript{3x}Li + Ph\textsubscript{2}SiX\textsubscript{2} \rightarrow Me\textsubscript{3}SiO(Me\textsubscript{2}SiO)\textsubscript{3x}Ph\textsubscript{2}SiX or alt. Me\textsubscript{3}SiOLi + x \text{D}_3 \rightarrow Me\textsubscript{3}SiO(Me\textsubscript{2}SiO)\textsubscript{3x}Li + acid \( \rightarrow \) Me\textsubscript{3}SiO(Me\textsubscript{2}SiO)\textsubscript{3x}H + Ph\textsubscript{2}SiX\textsubscript{2} \( \rightarrow \) Me\textsubscript{3}SiO(Me\textsubscript{2}SiO)\textsubscript{3x}Ph\textsubscript{2}SiX.
[0029] Step II of the present process is optional, but when selected involves processing the mixture to remove unreacted starting components or other volatile components. Typically, processing involves heating the reaction mixture to a temperature ranging from 25°C to 150°C, alternatively from 40° to 100°C, at reduced pressure while removing volatile species from the mixture under these conditions.

[0030] Step III involves reacting the \( R^5(R^1)_2SiOSi(R^3)_2OR^4 \) organosiloxane with

- c) an organohydrogensiloxane of the formula \( (R^1)_3SiO(R^1)(3-n)SiH \), and
- d) a hydrosilylation catalyst.

[0031] The organohydrogensiloxane used in step III has the formula \( (R^1)_3SiO(R^1)(3-n)SiH \), where \( R^1 \) and \( n \) are as defined above. Typically \( R^1 \) is methyl and \( n \) is 2, so that the organohydrogensiloxane has the formula \( (Me)_2SiO(Me)SiH \).

[0032] The reaction effected in step III is a hydrosilylation reaction, in which the SiH of the organohydrogensiloxane reacts with the unsaturated group present on \( R^5(R^1)_2SiOSi(R^3)_2OR^4 \) organosiloxane formed in step I of the present process to form an Si-C bond. The reaction may be conducted under those conditions known in the art for effecting hydrosilylations reactions.

[0033] The hydrosilylation reaction can be conducted neat or in the presence of a solvent. The solvent can be an alcohol such as methanol, ethanol, isopropanol, butanol, or n-propanol, a ketone such as acetone, methylethyl ketone, or methyl isobutyl ketone; an aromatic hydrocarbon such as benzene, toluene, or xylene; an aliphatic hydrocarbon such as heptane, hexane, or octane; a glycol ether such as propylene glycol methyl ether, dipropylene glycol methyl ether, propylene glycol n-butyl ether, propylene glycol n-propyl ether, or ethylene glycol n-butyl ether, a halogenated hydrocarbon such as dichloromethane, 1,1,1-trichloroethane or methylene chloride, chloroform, dimethyl sulfoxide, dimethyl formamide, acetonitrile, tetrahydrofuran, white spirits, mineral spirits, or naphtha.

[0034] The amount of solvent can be up to 70 weight percent, but is typically from 20 to 50 weight percent, said weight percent being based on the total weight of components in the hydrosilylation reaction. The solvent used during the hydrosilylation reaction can be subsequently removed by various known methods.
Additional components can be added to the hydrosilylation reaction which are known to enhance such reactions. These components include salts such as sodium acetate which have a buffering effect in combination with platinum catalysts.

The amounts of component c used in the hydrosilylation reaction vs the amount of the R^5(R^1)_{2}SiOSi(R^3)_{2}OR^4 organosiloxane may vary. The molar ratio of the SiH units of component c) to the unsaturated groups of the R^5(R^1)_{2}SiOSi(R^3)_{2}OR^4 organosiloxane may range from 10/1 to 1/10, alternatively from 5/1 to 1/5, or alternatively from 2/1 to 1/2.

Component d) is a hydrosilylation catalyst. The hydrosilylation catalyst may be any suitable Group VIII metal based catalyst selected from a platinum, rhodium, iridium, palladium or ruthenium. Group VIII metal containing catalysts useful to catalyze curing of the present compositions can be any of those known to catalyze reactions of silicon bonded hydrogen atoms with unsaturated hydrocarbon groups. The preferred Group VIII metal for use as a catalyst to effect cure of the present compositions by hydrosilylation is a platinum based catalyst. Some preferred platinum based hydrosilylation catalysts for curing the present composition are platinum metal, platinum compounds and platinum complexes. Suitable platinum catalysts are described in US 2,823,218 (commonly referred to as "Speier's catalyst") and U.S. Patent No. 3,923,705. The platinum catalyst may be "Karstedt's catalyst", which is described in Karstedt's U.S. Patent Nos. 3,715,334 and 3,814,730. Karstedt's catalyst is a platinum divinyl tetramethyl disiloxane complex typically containing about one-weight percent of platinum in a solvent such as toluene. Alternatively the platinum catalyst may be a reaction product of chloroplatinic acid and an organosilicon compound containing terminal aliphatic unsaturation, as described in U.S. Patent No. 3,419,593. Alternatively, the hydrosilylation catalyst is a neutralized complex of platinum chloride and divinyl tetramethyl disiloxane, as described in US 5,175,325. Further suitable hydrosilylation catalysts are described in, for example, U.S. Patents 3,159,601; 3,220,972; 3,296,291; 3,516,946; 3,989,668; 4,784,879; 5,036,117; and 5,175,325 and EP 0 347 895 Bl.

The hydrosilylation catalyst may be added in an amount equivalent to as little as 0.001 part by weight of elemental platinum group metal, per one million parts (ppm) of the total reaction composition. Typically, the concentration of the hydrosilylation catalyst in the reaction composition is that capable of providing the equivalent of at least 1 part per million of elemental platinum group metal. A catalyst concentration providing the equivalent of 1 to
alternatively 5 to 500, alternatively 10 to 100 parts per million of elemental platinum group metal may be used.

[0039] Step IV of the present process is optional, and involves further processing the reaction mixture of step III to remove any volatile components. Step IV may be effected in a similar manner as step II, as described above.

[0040] The present disclosure further provides a method for improving the compatibility of a polyheterosiloxane by using the present organosiloxanes of the formula

\[(R_{1}^{1}SiO)_{(3-n)}(R_{1}^{1})_{(3-n)}Si-R_{2}^{2}Si(R_{1}^{1})_{2}OSi(R_{3}^{3})_{2}X\]

as a siloxane component during the preparation of a polyheterosiloxane. In particular, the present organosiloxanes may be added as a siloxane component in the preparation of the polyheterosiloxanes, as described in WO201/002826. Specifically, WO201/002826 teaches a method for preparing a polyheterosiloxane having at least two non-Si metal elements comprising:

(A) a metal (M1) alkoxide,

(B) a silicon-containing material having hydrolyzable groups selected from

(B1) an organosiloxane, or

(B2) a silane, and

(C) a hydrolyzable metal (M2) salt,

with an amount of water that provides between 50 and 200% necessary to hydrolyze and condense the alkoxy groups and other hydrolyzable groups on Components (A), (B), and (C), to form the polyheterosiloxane. Thus, the present organosiloxanes of the formula

\[(R_{1}^{1}SiO)_{(3-n)}(R_{1}^{1})_{(3-n)}Si-R_{2}^{2}Si(R_{1}^{1})_{2}OSi(R_{3}^{3})_{2}X\]

may be used as all or part of component (B1) in the WO201/002826 method. The amount of the present organosiloxanes used as component B1 in the WO201/002826 method may vary from 0.05 weight percent to 100 weight percent of the total amount of organosiloxane added for the preparation of the polyheterosiloxane.
EXAMPLES

[0041] The following examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventor to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention. All percentages are in wt. %. All measurements were conducted at 23°C unless indicated otherwise.

Example 1

*Synthesis of (Me₃SiO)₂MeSiCH₂CH₂(CH₃)₂SiOSiPh₂(OMe)*

[0042] ViMe₂SiOSiPh₂(OMe) was first prepared by mixing 15.18g divinyltetramethyldisiloxane, 100.3g Ph₂Si(OMe)₂ and 0.40g triflic acid (FC-24) in a 1 liter flask and stirred for 1 hour at 50°C and 5 hours at RT. Then, 2.0g CaCO₃ was added to the flask and stirred at RT for overnight. Then, the mixture was pressure filtered through a 0.45µm filter. The recovered material was subjected to a rotary evaporation apparatus. ViMe₂Si(OMe) and unreacted divinyltetramethyldisiloxane were removed at 50-60°C and 0.3-0.5mmHg. 117.6 g material was collected in a 3-neck flask. The flask was heated to 90°C. Then, 0.1g 1% Pt was added to the flask. Under stirring, 70.8g (Me₃SiO)₂(Me)SiH was slowly added into the flask in approximately 30 minutes. Temperature rose to 122°C. FTIR was used to monitor the SiH content of the mixture after 15 minutes and found that the SiH was completely consumed. 1.6g (Me₃SiO)₂(Me)SiH was added to the flask and stirred at 110°C for 30 minutes. FTIR revealed a weak SiH peak at -2148 cm⁻¹. Heating mantle was removed and the flask was cooled to RT. A thin film evaporator (Pope Scientific) was used to purify the product. 1st run was set at 120°C and 0.4-0.5 mmHg. Unreacted Ph₂Si(OMe)₂ and small amount of (Me₃SiO)₂(Me)SiH were removed. 2nd run was set at 210°C and 0.4-0.5
mmHg. The product, \((\text{Me}_3\text{SiO})_2\text{MeSiCH}_2\text{CH}_2\text{SiOSiPh}_2(\text{OMe})\) was separated from yellow residue.

Example 2

*Synthesis of Si+Ti+Eu polyheterosiloxane using*

\((\text{Me}_3\text{SiO})_2\text{MeSiCH}_2\text{CH}_2(\text{CH}_3)_2\text{SiOSiPh}_2(\text{OMe})\)

[0043] 29.9 g europium 2-ethylhexanoate (10% in toluene) was transferred to a 100ml flask. 0.090 g 0.1 M HCl was added to the flask. It turned clear after stirring for 10 minutes. 1.0 g toluene and 4.40 g tetraisopropoxide (TPT) were added to the flask and stirred at 60°C for 40 minutes. Then added a prehydrolyzed monofunctional siloxane solution prepared by mixing 12.40 g \((\text{Me}_3\text{SiO})_2\text{MeSiCH}_2\text{CH}_2\text{SiOSiPh}_2(\text{OMe})\), 0.67 g 0.1 M HCl, and 9.0 g IPA and sonicating for 10 minutes at RT. The solution was clear and stirred at RT for 10 minutes. Volatile components were removed using a rotary evaporator at 60°C and 0.5 mmHg for 30 minutes. A clear yellow photoluminescent liquid was transferred to a glass vial. Eu element content was estimated to be 4.9% based on the weights of raw materials and final product. The product was compatible with polydimethylsiloxanes (350 cSt DOW CORNING® 200 fluid), vinyl-terminated polydimethylsiloxanes (DOW CORNING® SFD 119 Fluid), OH-terminated polydimethylsiloxanes (having a viscosity of 40 mm²/sec at 25°C), vinyl-terminated polyphenylmethylsiloxanes \((M^{\text{VI}}D^{\text{PhMe}}C_{2,5M}V_i)\), and OH-terminated polyphenylmethylsiloxanes (having a viscosity of 500 mm²/sec at 25°C).
Claims

1. An organosiloxane having the formula;

\[(R^1_3SiO)_n(R^1_3)_{3-n}Si-R^2Si(R^1)_2OSi(R^3)_2X\]

where \(n\) is 1 or 2,
- \(R^1\) is independently a monovalent \(C_1\) to \(C_{20}\) hydrocarbyl,
- \(R^2\) is a divalent \(C_2\) to \(C_{12}\) hydrocarbyl,
- \(R^3\) is independently a monovalent \(C_{30}\) hydrocarbyl containing at least one aryl group,
- \(X\) is a hydrolyzable group selected from
  - \(-OR^4\), \(-Cl\), \(-OC(0)R^4\), \(-N(R^4)_2\), or \(-ON=CR^4_2\)
  where \(R^4\) is hydrogen or a \(C_6\) alkyl group.

2. The organosiloxane of claim 1 where \(n\) is 2.

3. The organosiloxane of claim 1 or 2 where \(R^1\) is methyl (Me).

4. The organosiloxane of any one of the above claims where \(R^2\) is \(-CH_2CH_2\).

5. The organosiloxane of any one of the above claims where \(R^3\) is \(C_6H_5\).

6. The organosiloxane of any one of the above claims where \(X\) is \(-OMe\).

7. The organosiloxane of claim 1 having the formula;

\[(Me_3SiO)_2(Me)SiCH_2CH_2Si(CH_3)_2OSi(C_6H_5)_2(OMe)\].
8. A process for preparing an organosiloxane comprising:
   I) reacting;
      a) an organosilane of the formula \((\text{R}^3)\text{Si(OR}^4)\text{)}_2\)
          where \(\text{R}^3\) is independently a monovalent \(\text{C}_1\text{toC}_{30}\) hydrocarbyl
          containing at least one aryl group,
          \(\text{R}^4\) is hydrogen or a \(\text{C}_1\text{toC}_6\) alkyl group,
      b) a disiloxane of the formula \(\text{R}^5(\text{R}^1)\text{SiOSi(\text{R}^1)R}^5\)
          where \(\text{R}^1\) is independently a monovalent \(\text{C}_1\text{toC}_2\)hydrocarbyl,
          \(\text{R}^5\) is a \(\text{C}_2\text{toC}_{12}\) hydrocarbyl having a terminal unsaturated group,
          to form a mixture containing an organosiloxane of the formula
          \(\text{R}^8\text{R}^8\text{SiOSi}(\text{R}^3)\text{OR}^4\),
   II) optionally, processing the mixture to remove unreacted starting components or
       other volatile components,
   III) reacting the \(\text{R}^5(\text{R}^1)\text{SiOSi(\text{R}^3)\text{OR}^4}\) organosiloxane with
       c) an organohydrogensiloxane of the formula \((\text{R}^1\text{SiO})_n(\text{R}^1)\text{SiH})\)
          where \(\text{R}^1\) is independently a monovalent \(\text{C}_1\text{toC}_2\)hydrocarbyl,
          \(n\) is 1 or 2, alternatively \(n = 2\), and
       d) a hydrosilylation catalyst,
   IV) optionally, further processing the reaction mixture of step III to remove any
       volatile components.

9. The process of claim 8 where \(\text{R}^3\) is \(\text{C}_6\text{H}_{15}\).
10. The process of claim 8 or 9 where \(\text{R}^4\) is methyl.
11. The process of any one of claims 8 - 10 where \(\text{R}^1\) is methyl and \(\text{R}^5\) is \(\text{CH}_2=\text{CH}-\).
12. The product prepared according to any one of claims 8 - 11.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C07F7/18  C08G77/58  G02B1/04

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)

C07F  C08G  G02B

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**

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<tr>
<th>Category</th>
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<td>US 2012/094450 Al (DOW CORNING [US]; DOW CORNING TORAY CO LTD [JP]; AMAKO MASAAKI [JP]; I) 12 July 2012 (2012-07-12) Organopolysi oxanes of formula [\text{Ph (Me)Si 02/2}] \text{, [Ph3Si 03/2]} \text{, [RSi 03/2]} \text{, and [Ph (Me)Si 02/2]} \text{c[Ph3Si 03/2]} \text{, [RSi 03/2]} \text{d; claim 5}} \text{Use of polyheterosi oxanes to give curable refractive material s; claims 9-10}</td>
<td>1-12</td>
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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) one of which may be established under Article 49(2) PCT
  *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

**Date of the actual completion of the international search**

13 September 2013

**Name and mailing address of the ISA**

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk
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**Date of mailing of the international search report**

23/09/2013

**Authorized officer**

Lange, Tim

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<td></td>
<td>Silanol-containing organosilane, prepared from mixing Ph(Me)Si(0Me)2, PhSi(0Me)3, acid and transition metals; examples 1-33, 35-38; table 1</td>
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<td>Use of material to impart high ref index, impact resistance, scratch resistance etc.; page 1, paragraph 3</td>
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