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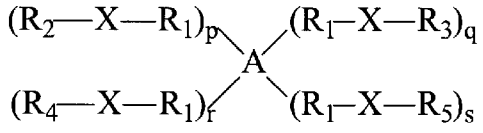
(54) **Title**: SILSESQUIOXANE DERIVATIVES HAVING SULFUR CONTAINING SUBSTITUENTS



(I)

(57) **Abstract**: The invention relates to a silsesquioxane compound of formula (I) having sulfur containing substituents, where A, R_1, R_2, R_3, R_4, R_5, X, p, q, r and s are as disclosed herein. Also, described are methods for their preparation and use as a lubricant.

WO 2010/101530 A1

SILSESQUIOXANE DERIVATIVES HAVING SULFUR CONTAINING SUBSTITUENTS

CROSS-REFERENCE TO RELATED APPLICATION

This application claims benefit of, and priority from, U.S. provisional application No. 61/202,492, filed on March 4, 2009, the contents of which are hereby incorporated herein by reference.

FIELD

The invention relates to silsesquioxane derivatives having sulfur containing substituents, their preparation methods and use as a lubricant.

BACKGROUND

Silsesquioxane is a compound having the empirical formula $RSiO_{1.5}$, where R is H or an organic substituent, such as alkyl, aryl, etc. Polyhedral oligomeric silsesquioxane (POS) molecules comprise silicon and oxygen atoms which are linked into well-defined regular structures, such as a cubic cage where the silicon atoms are at the corners. Among the POS structures, octameric silsesquioxane $[(RSiO_{1.5})_8]$ has generally received more attention and derivatives of it have been obtained. This is likely because of the well-defined cage structure, which has a nano-sized rigid inorganic core, and can be attached to eight functional groups to produce organic-inorganic hybrid structures. The POS structure has been employed as a pendant group for integration into a polymer backbone, to enhance the physical and mechanical properties of the polymer. The functionalization of POS corner substituents allows for development of a variety of materials that can be useful in different applications. For

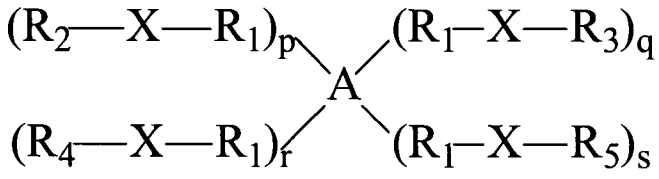
example, POS-containing materials produced may exhibit heat resistance, electrical insulation, flame resistance, and so on. They have been utilized for semiconductors, insulator materials, liquid crystalline materials, etc. WO 2008/017593 A1 discloses polyhedral oligomeric silsesquioxane based fluorescent colorants.

Lubricants have been proposed in the art for use at temperatures of up to 200°C or higher. High temperature lubricants can have applications in different industries, such as automotive and aerospace. These lubricants are primarily synthetic esters derived from various polyhydroxyl compounds and carboxylic acids. US 7,217,683 discloses polyhedral oligomeric silsesquioxane and polyhedral oligomeric silicates as lubricants.

SUMMARY

The invention relates to a silsesquioxane derivative having sulfur containing substituents, their preparation methods and use as a lubricant.

According to one aspect of the present invention, there is provided a compound of formula (I):



(I)

where

A is a silsesquioxane;

R_1 is $-(C(R^a)_2)_x-$ or $-O-Si(R^a)_2(C(R^a)_2)_x-$, where each x is independently an integer of 1 to 6 and each R^a is independently a H or C_1-C_6 alkyl (and in an exemplary

embodiment, $-CH_2-CH_2-$ or $-O-Si(Me)_2CH_2CH_2-$), wherein when R_1 is $-O-Si(R^a)_2(C(R^a)_2)_x-$, the O atom of R_1 bonds to Si on A;

X is S, SO, or SO_2;

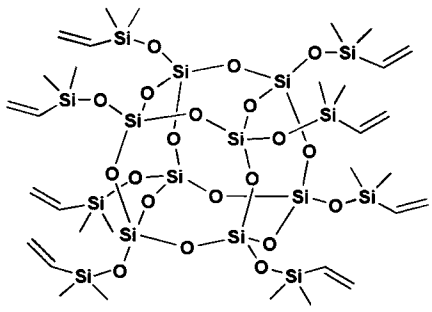
each R_2, R_3, R_4 and R_5, when present, is independently a linear or branched alkyl group of formula C_nH_{2n+1}, where n is from 1 to 30, or a group of formula $Ar(CH_2)_m-$, where Ar is a C_{6-10} aryl or a 5 to 10 membered heterocyclic group containing one or more heteroatoms, where each independently is N, O or S, and m is from 1 to 30, and

each p, q, r and s is independently from 0 to the total number of Si atoms in A, and the sum of p, q, r and s is from 4 to the total number of Si atoms in A.

Another aspect of the present invention are processes for preparing compounds of formula (I) as disclosed herein.

According to still a further aspect of the present invention, there is provided a lubricant comprising a compound of formula (I), as defined above.

According to yet another aspect of the present invention, there is provided the compound octa(vinyldimethylsilyl)-POS



Octa(vinyldimethylsilyl)-POS

BRIEF DESCRIPTION OF FIGURES

FIGURE 1 discloses the differential scanning calorimetry (DSC) curve of a POS oil - $(n\text{-}C_6H_{13}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$.

FIGURE 2 discloses the differential scanning calorimetry (DSC) curve of a POS oil - $(n\text{-}C_8H_{17}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$.

FIGURE 3 discloses the viscosity behavior of a POS oil - $(n\text{-}C_6H_{13}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$ at (I) 25 °C, (II)50 °C, and (III) 100 °C.

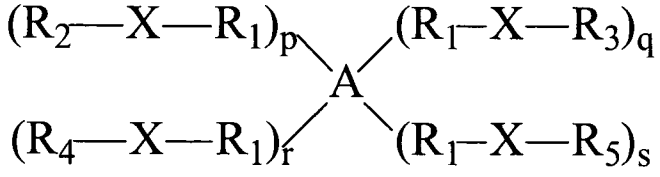
FIGURE 4 discloses the viscosity behavior of a POS oil - $(n\text{-}C_8H_{17}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$ at (I) 25 °C, (II)50 °C, and (III) 100 °C.

FIGURE 5 discloses the thermal aging effect on the thermal stability of POS oil measured by thermal gravimetric analysis (TGA).

DETAILED DESCRIPTION

The invention relates to silsesquioxane derivatives having sulfur containing substituents, their preparation methods and use as a lubricant.

As described above, the present invention provides a compound of formula (I)

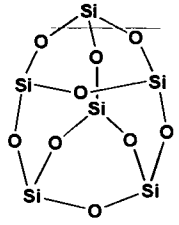


(I)

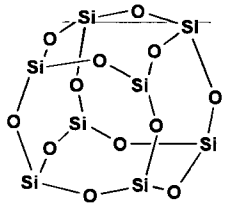
where

A, X, R_1, R_2, R_3, R_4, p, q, r and s are as defined above.

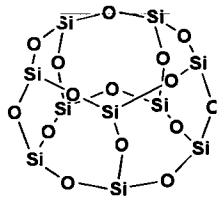
In one embodiment, the substituent A in the compound of formula (I) is a polyhedral oligomeric silsesquioxane (POS). For example, the POS may be



$(SiO_{1.5})_6$

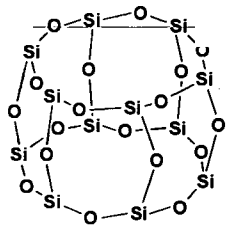


$(SiO_{1.5})_8$



$(SiO_{1.5})_{10}$

or



$(SiO_{1.5})_{12}$

In an exemplary embodiment, the POS may be $(SiO_{1.5})_8$.

In another embodiment, R_1 in the compound of formula (I) is $-CH_2-CH_2-$ or $-OSi(Me)_2CH_2CH_2-$, which bonds to a Si atom in the silsesquioxane. When R_1 is $-OSi(Me)_2CH_2CH_2-$, the O atom bonds to the Si atom of the silsesquioxane. It will be understood that R_1 binds to the silicon atom of A.

In still another embodiment, each R_2, R_3, R_4 and R_5, when present, is independently a linear or branched alkyl group of formula C_2H_{2n+1}, where n is from 1 to 30, or a group of formula $Ar(CH_2)_m-$, where Ar is a C_{6-10} aryl group or a 5 to 10 membered heterocyclic group containing one or more heteroatoms, where each independently is N, O or S, and m is from 1 to 30. It will be understood that the 5 to 10 membered heterocyclic group may be a non-aromatic heterocyclic group or an aromatic heterocyclic group.

In yet another embodiment, the sum of p, q, r and s is 6, 8, 10 or 12.

For purposes of illustration, the C_{1-6} alkyl group, which is representative of the linear or branched alkyl group of formula C_2H_{2n+1}, may be, for example, methyl, ethyl, n-propyl, i-propyl, sec-propyl, n-butyl, i-butyl, sec-butyl, t-butyl, n-pentyl, i-pentyl, sec-pentyl, t-pentyl, n-hexyl,

i-hexyl, 1,2-dimethylpropyl, 2-ethylpropyl, 1-methyl-2-ethylpropyl, 1-ethyl-2-methylpropyl, 1,1,2-trimethylpropyl, 1,1-dimethylbutyl, 2,2-dimethylbutyl, 2-ethylbutyl, 1,3-dimethylbutyl, 2-methylpentyl or 3-methylpentyl.

For purposes of illustration, the C_{6-10} aryl group, may be, for example, phenyl, indenyl, naphthyl, or azulenyl.

For purposes of illustration, the 5- to 10-membered non-aromatic heterocyclic group, may be, for example, pyrrolidinyl, pyrrolinyl, piperidinyl, piperazinyl, imidazolinyl, pyrazolidinyl, imidazolydinyl, morpholinyl, tetrahydropyranyl, oxathiolanyl, phthalimide or succinimide.

For purposes of illustration, the 5- to 10-membered aromatic heterocyclic, may be, for example, pyrrolyl, pyridinyl, pyridazinyl, pyrimidinyl, pyrazinyl, imidazolyl, thiazolyl or oxazolyl.

For purposes of illustration, the group of formula $Ar(CH_2)_m$-, where Ar is a C_{6-10} aryl or a 5 to 10 membered heterocyclic group , may comprise, for example, an alkyl as disclosed herein and having a C_{6-10} aryl or a 5 to 10 membered heterocyclic group as disclosed herein.

In another aspect of the invention, disclosed is a process for the preparation of a compound of formula (I), by reacting a compound of formula (I') or (I''') with R'-SH, in the presence of a radical initiator,

$A-(CH=CH_2)_{p+q+r+s}$ (I') or $A-(OSi(Me)_2CH=CH_2)_{p+q+r+s}$ (I''')

wherein A is as defined above, and R' is R_2, R_3, R_4 or R_5, as defined above, or R'-SH comprises a mixture of compounds having different R' groups.

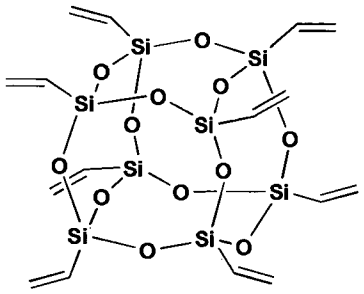
In still another aspect of the invention, disclosed is a process for the preparation of a compound of formula (I), by reacting a compound of formula (I'') or (I''''') with R'', in the presence of a radical initiator,

$$A\text{-}(CH_2CH_2\text{-}SH)_{p+q+r+s} \quad (I'') \quad \text{or}$$

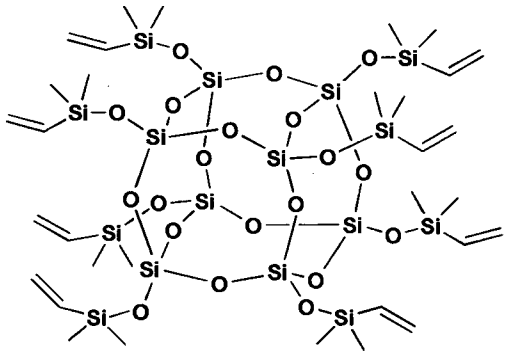
$$A\text{-}(OSi(Me)_2CH_2CH_2SH)_{p+q+r+s} \quad (I''''')$$

wherein A is a defined above, R'' is a precursor of R_2, R_3, R_4 or R_5, as defined above, and has a terminal unsaturated bond.

For the purpose of illustration, R_1' is a vinyl group. For example, the compound of formula (I') or (I''') is



or

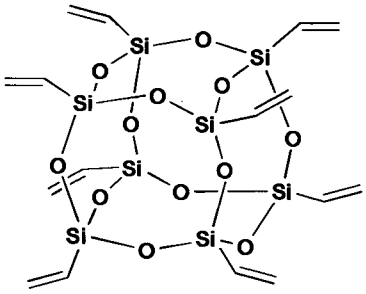


Octa(vinyl)-POS Octa(vinyldimethylsilyl)-POS

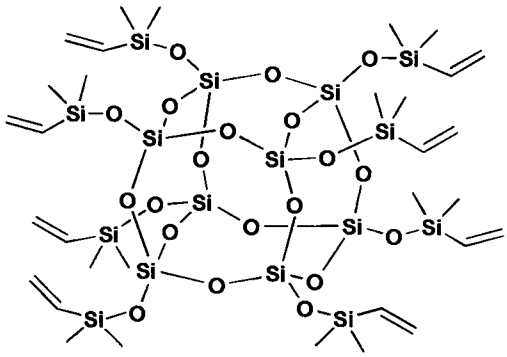
For purpose of illustration, R'' is, for example a terminal alkene, such as 1-octene.

In the process for preparation of a compound of formula (I), A may be POS. In the family of POS structures, such as $(RSiO_{1.5})_6$, $(RSiO_{1.5})_8$, $(RSiO_{1.5})_{10}$, and $(RSiO_{1.5})_{12}$), the octameric POS structure ($(RSiO_{1.5})_8$) is generally understood to have good stability, facile synthesis and may be easily modified. The POS structures may be formed from hydrolysis or condensation reactions of simple $RSiCl_3$ or $RSi(OR)_3$ silanes where R is an aliphatic or an aromatic group. For instance, octameric silsesquioxane may be prepared in this

way. The POS compounds may be synthesized by chemical modification of several functionalized POS precursors that possess reactive functional groups, such as a C=C double bond, as shown below. These functional groups allow for further chemical modification to prepare POS compounds having different properties.

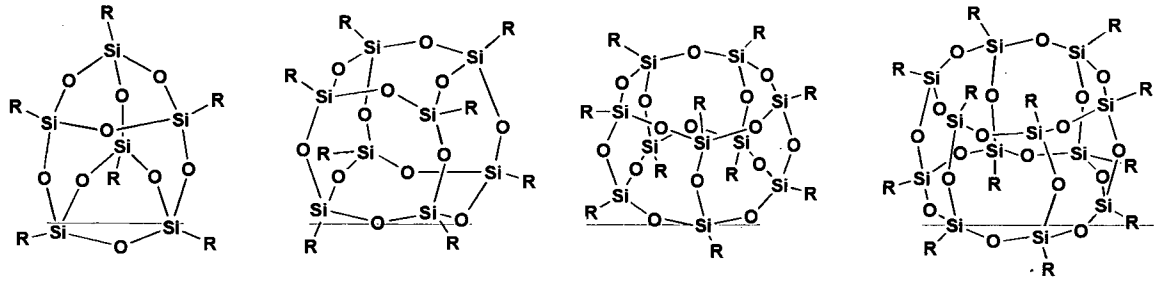


Octa(vinyl)-POS



Octa(vinyldimethylsilyl)-POS

In yet another aspect of the present invention, there is provided a lubricant (a "POS lubricant") comprising the compound of formula (I), as defined above. POS lubricants of the invention may be prepared by reacting octa(vinyl)-POS or octa(vinyldimethylsilyl)-POS with various thiol compounds in the presence of free radical initiators such as 2,2-azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), etc. The thiol compounds may be linear or branched (e.g., R'-SH). The free radical addition reaction usually completes within 3-5 hours as monitored by ^{1}H nuclear magnetic resonance (NMR) spectroscopy. Representative chemical structures of POS lubricants are shown below.



$(RSiO_{1.5})_6$ $(RSiO_{1.5})_8$ $(RSiO_{1.5})_{10}$ $(RSiO_{1.5})_{12}$

Example of Homoleptic POSS Derivatives $[RSiO_{1.5}]_{6, 8, 10, or 12}$
R = CH_2CH_2SR'; $OSi(Me)_2CH_2CH_2SR'$

When preparing a POS lubricant, the desired amount of POS and thiol compound is placed into a reaction vessel. The thiol compound is added in the reaction mixture in an excess of 0 mol %-100 mol % relative to the amount of POS. After the addition reaction is complete, the excess thiol compound can be recovered by vacuum distillation when the product is a liquid or by washing with a suitable organic solvent including acetonitrile, acetone, methanol, etc. when the product is a solid. The reaction time is generally dependent upon the type and length of the alkyl group of the thiol compound. In general, the larger the size of the alkyl group of the thiol compound, the longer the reaction time. For example, the reaction time is generally less than 5 hours when the number of carbon atoms of the thiol compound is not more than 12. Radical initiators can be chosen from azos and peroxides, such as AIBN and BPO, with AIBN being an exemplary initiator. The reaction may be carried out in an organic solvent including benzene, toluene, xylene, etc, but usually in the absence of any organic solvents, particularly when the product is a liquid and the number of carbon atoms in the thiol compound is not more than 12. POS lubricants with different corner substituents can be synthesized by reacting a mixture of thiol compounds with octa(vinyl)-POS or octa(vinyldimethylsilyl)-POS. For example, a mixture of compounds of the average general formula

$(n\text{-}C_6H_{13}SCH_2CH_2Si(Me)_2OSiO_{1.5})_4(n\text{-}C_8H_{17}SCH_2CH_2Si(Me)_2OSiO_{1.5})_4$ can be prepared by heating $n\text{-}C_6H_{13}SH$, $n\text{-}C_8H_{17}SH$ and octa(vinyldimethylsilyl)-POS in a molar ratio of 6:6:1, respectively, in the presence of AIBN at 80°C. In another embodiment, a mixture of the compounds of average general formula $(n\text{-}C_6H_{13}SCH_2CH_2SiO_{1.5})_4(n\text{-}C_8H_{17}SCH_2CH_2SiO_{1.5})_4$ can be prepared by heating $n\text{-}C_6H_{13}SH$, $n\text{-}C_8H_{17}SH$ and octa(vinyl)-POS in a molar ratio of 6:6:1, respectively, in the presence of AIBN at 80°C. Other combinations of POS lubricant can be obtained following a similar synthetic method to those described above. The reaction conversion estimated based on the POS reactant is almost quantitative. Observed, isolated synthetic yields have been more than 99%. Moreover, the product is chemically pure enough for further characterization after removal of the excess thiol reactant.

Similar to traditional lubricants, the viscosity of POS derivatives has been observed to behave like a Newtonian liquid. The dynamic viscosity of POS lubricants derived from octa(vinyldimethylsilyl)-POS is around 0.15-0.17 Pas at 25°C. The dynamic viscosity drops to around 0.053-0.066 Pas at 50°C and further goes down to around 0.017-0.019 Pas at 100°C (Table 1). In contrast, a lubricant derived from oct(vinyl)-POS shows a relatively higher dynamic viscosity, likely due to the more rigid structure. The surface tension for POS oil has been observed to be relative to the length of corner chains, ranging from 27.7-31.3 mNm^{-1} (Table 2). In principle, the introduction of flexible chains to POS structures leads to a reduction of the melting point. POS derivatives $(n\text{-}C_6H_{13}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$ and $(n\text{-}C_8H_{17}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$ have been observed to have freezing and melting points of less than - 80°C (Figures 1 and 2).

TABLE 1

Tabulated viscosity data for selected POS lubricants

Composition	Viscosity (Pas) at 25°C	Viscosity (Pas) at 50°C	Viscosity (Pas) at 100°C
~~$(n\text{-}C_6H_{13}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$~~	~~0.16~~	~~0.054~~	~~0.017~~
$(n\text{-}C_8H_{17}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	0.15	0.053	0.017
$(n\text{-}C_{10}H_{21}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	0.17	0.066	0.017
$(n\text{-}C_{12}H_{25}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	0.17	0.066	0.019
$(n\text{-}C_6H_{13}SCH_2CH_2SiO_{1.5})_8$	0.25	0.087	0.021

TABLE 2

Tabulated physical properties for selected POS lubricants

Composition	Density (gcm^{-3})	Surface tension (mNm^{-1})	Freezing point (°C)	Melting point (°C)
$(n\text{-}C_6H_{13}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	1.06	27.7	< -80	< -80
$(n\text{-}C_8H_{17}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	1.04	29.8	< -80	< -80
$(n\text{-}C_{10}H_{21}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	1.02	31.3	-40	-26 ~ -9
$(n\text{-}C_{12}H_{25}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	1.00	31.3	-7	2 ~ 10

TGA experiments were conducted to observe the relative thermal stability of POS lubricants. The decomposition temperature is defined as the temperature at which 5% weight loss occurs. For POS products derived form octa(vinyldimethylsilyl)-POS, their decomposition temperatures were measured at between 340-402 °C in air and nitrogen (Table 3). For POS product derived form octa(vinyl)-POS, the decomposition temperature was observed to be between 337-400 °C in air and nitrogen (Table 4). Both of these two series of POS derivatives display high decomposition temperatures. The thermal aging tests were conducted by using a similar amount of the compounds (15-18 mg), which is placed on a sample holder and is heated at 220°C for about 500 min. All POS lubricants were observed

to have thermal stability with a range of weight loss of 2.25%-7.25%.

TABLE 3

Tabulated TGA Data for POS lubricant

Composition	N_2 (°C)	Residue (%) at 900°C	Air (°C)	Residue (%) at 900°C
$(n\text{-}C_6H_{13}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	378	35.0	360	30.0
$(n\text{-}C_8H_{17}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	368	31.0	338	26.5
$(n\text{-}C_{10}H_{21}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	400	26.9	357	24.1
$(n\text{-}C_{12}H_{25}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	400	24.4	353	21.3
$(n\text{-}C_{14}H_{29}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	385	18.3	357	17.0
$(n\text{-}C_{16}H_{33}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	363	19.6	337	17.8
$(n\text{-}C_{18}H_{35}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	360	16.1	362	17.2

TABLE 4

Tabulated TGA Data for POS lubricant

Composition	Nitrogen (°C)	Residue (%) at 900°C	Air (°C)	Residue (%) at 900°C
$(n\text{-}C_6H_{13}SCH_2CH_2SiO_{1.5})_8$	387	37.3	372	41.0
$(n\text{-}C_8H_{17}SCH_2CH_2SiO_{1.5})_8$	382	33.8	358	37.4
$(n\text{-}C_{10}H_{21}SCH_2CH_2SiO_{1.5})_8$	402	31.7	384	35.2
$(n\text{-}C_{12}H_{25}SCH_2CH_2SiO_{1.5})_8$	373	31.5	360	32.0
$(n\text{-}C_{14}H_{29}SCH_2CH_2SiO_{1.5})_8$	385	26.0	341	28.0
$(n\text{-}C_{16}H_{33}SCH_2CH_2SiO_{1.5})_8$	354	24.2	342	27.0
$(n\text{-}C_{18}H_{35}SCH_2CH_2SiO_{1.5})_8$	373	23.5	340	26.5

It is desired that a high temperature lubricant composition possess a low evaporation loss and not form deposits or varnish when exposed to high temperature environments for a given time period. In order to measure the evaporation loss of the lubricant at a specific temperature, a lubricant sample is maintained in an oven at the specific temperature for an extended period of time and

the weight loss is then determined. Evaporation loss, deposit formation tendency, and residual oil fluidity are evaluated using the following procedure: one gram of lubricant is placed in a glass vial. The test condition at a specific temperature is held for a few hours or few days. Evaporation loss, deposit formation tendency, and flow properties of the lubricant after this procedure are measured by weight and by visual observation, respectively. The evaporation loss was calculated according to the following formula:

$$\text{Evaporation loss (\%)} = \frac{\text{weight loss after heating}}{\text{initial weight of lubricant before heating}} \times 100\%$$

The POS lubricants provided by the present invention have been observed to have slow evaporation loss values under the measured temperature. For instance, the evaporation loss for POS derivative $(n\text{-}C_6H_{13}SCH_2CH_2Si(Me)_2SiO_{1.5})_8$ at 218 °C for 24 h was 2.5% and no deposit was observed. Even after heating for 96 h, it was still a liquid and only 11% had evaporated (Table 5). The POS lubricant $(n\text{-}C_{12}H_{25}SCH_2CH_2OSi(Me)_2OSiO_{1.5})_8$ demonstrated the lowest evaporation loss (7.7%) and it remained fluid after heating for 115h at 218 °C. Isothermal experiments at higher temperature of 288 °C were carried out and the lowest evaporation loss (0.7%) was observed for lubricant $(n\text{-}C_{12}H_{25}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$ (Table 5). The lubricant $(n\text{-}C_{12}H_{25}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$ exhibited the highest temperature performance among the four lubricants listed in Table 6.

TABLE 5

Tabulated weight loss after thermal aging at 218 °C							
Composition\weight loss	9h	24h	48h	72h	96h	115h	163h
$(n\text{-}C_6H_{13}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	1.1	2.5	5.9	8.9	11.0		15.8
$(n\text{-}C_8H_{17}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$		2.5	5.6			12.2	
$(n\text{-}C_{10}H_{21}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$		1.9	4.6			10.8	
$(n\text{-}C_{12}H_{25}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$		1.2	3.4			7.7	

TABLE 6

Tabulated thermal aging data at 288 °C for 5.5 hours			
Composition	weight loss	Deposit, visual	Fluidity, visual
$(n\text{-}C_6H_{13}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	7.7%	Not observed	Fluid
$(n\text{-}C_8H_{17}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	5.6%	Not observed	Fluid
$(n\text{-}C_{10}H_{21}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	4.2%	Not observed	Fluid
$(n\text{-}C_{12}H_{25}SCH_2CH_2Si(CH_3)_2OSiO_{1.5})_8$	0.7%	Not observed	Fluid

EXAMPLES

The following examples are intended as exemplary only and not in any way intended to limit the scope of the present invention.

EXAMPLE 1

Preparation of $(n\text{-}C_6H_{13}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$

A potion of octa(vinyldimethylsilyl)silsesquioxane (20.016 g, 163.0 mmol) was placed into a two-necked round-bottom flask equipped with a magnetic stirrer. 1-Hexylthiol (23.128 g, 195.6 mmol) was added to POS and the mixture was stirred and purged with pure nitrogen gas for half an hour. A catalytic amount of 2,2-azobis(isobutylcyanate) (AIBN) (322 mg) was added and the mixture was allowed to continue to purge nitrogen for another 15 minutes. Then the mixture

was heated up to 80°C and maintained at this temperature for 5 hours. After that, the reaction mixture was subject to NMR analysis. The characteristic signals of vinyl units in POS starting materials at 5.73-6.18 ppm disappeared, indicating the completeness of the reaction. The crude product was then vacuum-distilled to recover unreacted 1-hexylthiol and then to afford a light yellow oily liquid (35.21 g; yield, 99.3 %). The product was pure enough for further chemical analysis.

^{1}HNMR δ 2.62 ~ 2.56 (m, 16H), 2.51 (t, 16H), 1.59 ~ 1.54 (m, 16H), 1.43 ~ 1.23 (m, 48H), 1.00 ~ 0.96 (m, 16H), 0.91 (t, 24H), 0.19 (s, 48H). ^{13}C NMR δ 32.34, 31.85, 29.91, 29.05, 26.89, 22.93, 18.85, 14.39, 0.17. ^{29}Si NMR: δ 11.74, -108.92. MALDI-TOF MS Calc. $C_{80}H_{184}Si_{16}O_{20}S_8$: 2172.22. Observed: $[M+Ag]^+$, 2279.90.

EXAMPLE 2

Preparation of $(n\text{-}C_8H_{17}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$

Following the procedures outlined in Example 1, octa(vinyldimethylsilyl)silsesquioxane (20.017 g) was reacted with 1-octylthiol (28.614 g) to afford the product as a light yellow oily liquid (39.12 g; yield, 99.7%). ^{1}HNMR δ 2.60 ~ 2.56 (m, 16H), 2.51 (t, 16H), 1.59 ~ 1.55 (m, 16H), 1.42 ~ 1.20 (m, 80H), 1.00 ~ 0.97 (m, 16H), 0.90 (t, 24H), 0.19 (s, 48H). δ ^{13}C NMR δ 32.36, 32.21, 29.95, 29.60, 29.40, 26.90, 23.01, 18.86, 14.43, 0.17. ^{29}Si NMR δ 11.73, -108.92. MALDI-TOF MS Calc. $C_{96}H_{216}Si_{16}O_{20}S_8$: 2396.65. Observed: $[M+Ag]^+$, 2504.02

EXAMPLE 3

Preparation of $(n\text{-}C_{10}H_{21}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$

Following the procedures outlined in Example 1, octa(vinyldimethylsilyl)silsesquioxane (18.025 g) was reacted with 1-decylthiol (25.628 g) to afford the product

as a light yellow oily liquid (38.33 g; yield, 99.5%). ^{1}HNMR: δ 2.60 ~ 2.54 (m, 16H), 2.51(t, 16H), 1.61 ~ 1.53 (m, 16H), 1.42 ~ 1.21 (m, 112H), 1.00 ~ 0.97 (m, 16H), 0.88 (t, 24H), 0.19 (s, 48H). ^{13}C NMR δ 32.44, 32.33, 30.02, 29.74, 29.48, 26.98, 23.09, 18.92, 14.49, 0.23. ^{29}Si NMR δ 11.76, -108.91. MALDI-TOF MS Calc. $C_{112}H_{248}Si_{16}O_{20}S_8$: 2621.08. Observed: $[M+Ag]^+$, 2729.32

EXAMPLE 4

Preparation of $(n\text{-}C_{12}H_{25}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$

Following the procedures outlined in Example 1, octa(vinyldimethylsilyl)silsesquioxane (15.016 g) was reacted with 1-dodecylthiol (29.70 g) to afford the product as a light yellow oily liquid (34.57 g; yield, 99.2%). ^{1}HNMR δ 2.60 ~ 2.54 (m, 16H), 2.51 (t, 16H), 1.60 ~ 1.53 (m, 16H), 1.40 ~ 1.20 (m, 144H), 1.00 ~ 0.97 (m, 16H), 0.88 (t, 24H), 0.19 (s, 48H). ^{13}C NMR δ 32.40, 32.32, 30.04, 30.01, 29.74, 29.46, 26.94, 23.07, 18.88, 14.47, 0.20. ^{29}Si NMR δ 11.76, -108.90. MALDI-TOF MS Calc. $C_{128}H_{280}Si_{16}O_{20}S_8$: 2845.52. Observed: $[M+Ag]^+$, 2953.88.

EXAMPLE 5

Preparation of $(n\text{-}C_{14}H_{29}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$

A potion of octa(vinyldimethylsilyl)silsesquioxane (0.5 g, 0.79 mmol) and 1-tetradecylthoil (2.184 g, 9.48 mmol) were placed into a two-necked round-bottom flask with 50 ml of toluene. The flask was equipped with a magnetic stirrer and purged with pure nitrogen gas for half an hour. A catalytic amount of AIBN (15.55 mg) was then added and the mixture was allowed to continue to purge nitrogen for another 15 minutes. Then the mixture was heated up to 80°C and this temperature was maintained overnight (18 hours). After that, the reaction mixture was subject to NMR analysis. The characteristic signals of vinyl units in POS starting

materials at 5.73-6.18 ppm disappeared, indicating the completeness of the reaction. The solvent acetone was added to the reaction mixture, and the resulting white solid was filtered and collected as a white solid after washing with acetone. The product was pure enough for further chemical analysis. ^{1}HNMR δ 2.60 ~ 2.56 (m, 16H), 2.51 (t, 16H), 1.60 ~ 1.55 (m, 16H), 1.42 ~ 1.20 (m, 176H), 1.00 ~ 0.96 (m, 16H), 0.90 (t, 24H), 0.19 (s, 48H). ^{13}C NMR δ 32.44, 32.31, 30.08, 29.74, 29.47, 26.97, 23.06, 18.90, 14.45, 0.21. ^{29}Si NMR δ 11.76, -108.88. MALDI-TOF MS Calc. $C_{144}H_{312}Si_{16}O_{20}S_8$: 3069.95. Observed: $[M+Ag]^+$, 3178.90

EXAMPLE 6

Preparation of $(n\text{-}C_{16}H_{33}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$ and $(n\text{-}C_{18}H_{37}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$

Following the procedures outlined in Example 5, $(n\text{-}C_{16}H_{33}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$ and $(n\text{-}C_{18}H_{37}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$ were prepared.

$(n\text{-}C_{16}H_{33}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$: ^{1}HNMR δ 2.60 ~ 2.56 (m, 16H), 2.51 (t, 16H), 1.59 ~ 1.53 (m, 16H), 1.42 ~ 1.20 (m, 208H), 1.00 ~ 0.96 (m, 16H), 0.88 (t, 24H), 0.19 (s, 48H). ^{13}C NMR δ 32.42, 32.32, 30.08, 29.74, 29.46, 26.96, 23.06, 18.90, 14.45, 0.20. ^{29}Si NMR δ 11.78, -108.86. MALDI-TOF MS Calc. $C_{160}H_{344}Si_{16}O_{20}S_8$: 3294.38. Observed: $[M+Ag]^+$, 3403.51.

$(n\text{-}C_{18}H_{37}SCH_2CH_2Si(Me)_2OSiO_{1.5})_8$: ^{1}HNMR δ 2.60 ~ 2.56 (m, 16H), 2.51 (t, 16H), 1.59 ~ 1.53 (m, 16H), 1.42 ~ 1.20 (m, 240H), 1.00 ~ 0.96 (m, 16H), 0.88 (t, 24H), 0.19 (s, 48H). ^{13}C NMR δ 32.40, 32.32, 30.10, 29.74, 29.46, 26.93, 23.06, 18.88, 14.45, 0.19. ^{29}Si NMR δ 11.77, -108.88. MALDI-TOF MS Calc. $C_{176}H_{376}Si_{16}O_{20}S_8$: 3518.81. Observed: $[M+Ag]^+$, 3627.87.

EXAMPLE 7

Preparation of $(n\text{-}C_6H_{13}SCH_2CH_2SiO_{1.5})_8$

A potion of octa(vinyl)silsesquioxane (20.05 g, 31.67 mmol) was placed into a two-necked round-bottom flask equipped with a magnetic stirrer. 1-Hexylthiol (37.44 g, 316.7 mmol) was added to POS and the mixture was stirred and purged with pure nitrogen for half an hour. A catalytic amount of AIBN (520 mg) was added and the mixture was allowed to continue to purge nitrogen for another 15 minutes. Then the mixture was heated up to 80°C and maintained at this temperature for 5 hours. After that, the reaction mixture was subject to NMR analysis. The characteristic signals of vinyl units in POS starting materials at 5.73-6.18 ppm disappeared, indicating the completeness of the reaction. The crude product was then vacuum-distilled to remove the unreacted 1-hexylthiol and the residue was a light yellow oily liquid (49.50 g, yield, 99%). The product was pure enough for further chemical analysis. ^{1}HNMR δ 2.62-2.57 (m, 16H), 2.52 (t, 16H), 1.62-1.53 (m, 16H), 1.42-1.24 (m, 48H), 1.04-0.99 (m, 16H), 0.90 (t, 24H). ^{13}C NMR δ 32.35, 31.85, 29.89, 29.06, 26.37, 22.96, 14.39, 13.47 ^{29}Si NMR δ -68.58. MALDI-TOF MS Calc. $C_{64}H_{136}Si_8O_{12}S_8$: 1578.98. Observed: $[M+Ag]^+$, 1687.11.

EXAMPLE 8

Preparation of $(n\text{-}C_8H_{17}SCH_2CH_2SiO_{1.5})_8$

A potion of octa(vinyl)silsesquioxane (0.5 g, 0.79 mmol) was placed into a two-necked round-bottom flask equipped with a magnetic stirrer. 1-Octylthiol (1.155 g, 7.9 mmol) was added to POS and the mixture was stirred and purged with pure nitrogen gas for half an hour. A catalytic amount of AIBN (13 mg) was added and the mixture was allowed to continue to purge nitrogen for another 15 minutes. Then the mixture was heated up to 80°C and maintained at this temperature for 5 hours. After that, the reaction mixture was subject to NMR

analysis. The characteristic signals of vinyl units in POS starting materials at 5.73-6.18 ppm disappeared, indicating the completeness of the reaction. The crude product was then vacuum-distilled to remove the unreacted 1-octylthiol and the residue was collected after washing with a bit of acetone. The product was pure enough for further chemical analysis. ^{1}HNMR δ 2.62-2.57 (m, 16H), 2.51 (t, 16H), 1.62-1.53 (m, 16H), 1.42-1.22 (m, 80H), 1.03-0.99 (m, 16H), 0.88 (t, 24H). ^{13}C NMR δ32.30, 32.19, 29.91, 29.59, 29.37, 26.31, 23.00, 14.41, 13.41. ^{29}Si NMR δ -68.67. MALDI-TOF MS Calc. $C_{64}H_{136}Si_8O_{12}S_8$: 1803.41. Observed: $[M+Ag]^+$, 1911.18.

EXAMPLE 9

Following the procedures outlined in Example 5, **$(n\text{-}C_{10}H_{21}SCH_2CH_2SiO_{1.5})_8$**, **$(n\text{-}C_{12}H_{25}SCH_2CH_2SiO_{1.5})_8$**, **$(n\text{-}C_{14}H_{29}SCH_2CH_2SiO_{1.5})_8$**, **$(n\text{-}C_{16}H_{33}SCH_2CH_2SiO_{1.5})_8$**, **$(n\text{-}C_{18}H_{37}SCH_2CH_2SiO_{1.5})_8$** are prepared.

$(n\text{-}C_{10}H_{21}SCH_2CH_2SiO_{1.5})_8$: ^{1}HNMR δ 2.64-2.57 (m, 16H), 2.51 (t, 16H), 1.62-1.53 (m, 16H), 1.42-1.22 (m, 112H), 1.03-0.99 (m, 16H), 0.88 (t, 24H). ^{13}C NMR δ 32.34, 32.28, 29.97, 29.70, 29.42, 23.04, 14.45, 13.44. ^{29}Si NMR δ -68.65. MALDI-TOF MS Calc. $C_{80}H_{168}Si_8O_{12}S_8$: 2027.85. Observed: $[M+Ag]^+$, 2135.42.

$(n\text{-}C_{12}H_{25}SCH_2CH_2SiO_{1.5})_8$: ^{1}HNMR δ 2.64-2.54 (m, 16H), 2.51 (t, 16H), 1.64-1.53 (m, 16H), 1.41-1.22 (m, 144H), 1.03-0.99 (m, 16H), 0.88 (t, 24H).^{13}C NMR δ 32.36, 32.31, 30.03, 29.73, 29.45, 26.37, 23.06, 14.46, 13.45. ^{29}Si NMR δ -68.63. MALDI-TOF MS Calc. $C_{96}H_{200}Si_8O_{12}S_8$: 2252.28. Observed: $[M+Ag]^+$, 2360.84.

$(n\text{-}C_{14}H_{29}SCH_2CH_2SiO_{1.5})_8$: ^{1}HNMR δ 2.62-2.57 (m, 16H), 2.51 (t, 16H), 1.62-1.53 (m, 16H), 1.42-1.21 (m, 176H), 1.03-0.99 (m, 16H), 0.88 (t, 24H). ^{13}C NMR δ 32.34, 32.31, 30.07, 30.05,

29.96, 29.73, 29.43, 26.34, 23.05, 14.45, 13.43. ^{29}Si NMR δ -68.58. MALDI-TOF MS Calc. $C_{112}H_{232}Si_8O_{12}S_8$: 2476.71. Observed: $[M+Ag]^+$, 3033.87.

$(n\text{-}C_{16}H_{33}SCH_2CH_2SiO_{1.5})_8$: ^{1}HNMR δ 2.61-2.57 (m, 16H), 2.51 (t, 16H), 1.62-1.52 (m, 16H), 1.42-1.20 (m, 208H), 1.04-0.99 (m, 16H), 0.88 (t, 24H) ^{13}C NMR δ 32.40, 32.31, 30.09, 29.74, 29.47, 26.39, 23.06, 14.45, 13.47. ^{29}Si NMR δ -68.58. MALDI-TOF MS Calc. $C_{144}H_{296}Si_8O_{12}S_8$: 2701.14. Observed: $[M+Ag]^+$, 2809.72.

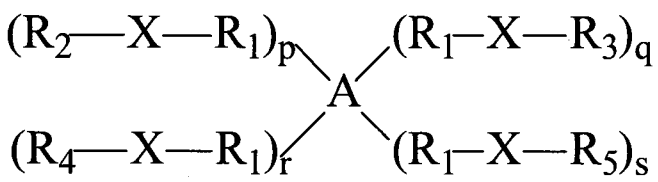
$(n\text{-}C_{18}H_{37}SCH_2CH_2SiO_{1.5})_8$: ^{1}HNMR δ 2.61-2.57 (m, 16H), 2.51 (t, 16H), 1.62-1.52 (m, 16H), 1.42-1.20 (m, 240H), 1.01(t, 16H), 0.88 (t, 24H). δ ^{13}C NMR δ 32.42, 32.31, 30.10, 29.74, 29.47, 26.42, 23.05, 14.44, 13.49. ^{29}Si NMR δ -68.59. MALDI-TOF MS Calc. $C_{160}H_{328}Si_8O_{12}S_8$: 2925.57. Observed: $[M+Ag]^+$, 3033.55.

EXAMPLE 10

Following the procedures outlined in Example 1, **$(n\text{-}C_6H_{13}SCH_2CH_2SiO_{1.5})_4(n\text{-}C_8H_{17}SCH_2CH_2SiO_{1.5})_4$** was prepared. ^{1}HNMR δ 2.59 (t, 16H), 1.61-1.53 (m, 16H), 1.45-1.20 (m, 64H), 1.01 (t, 16H), 0.88 (m, 24H).

CLAIMS:

1. A compound of formula (I):



(I)

where

A is a silsesquioxane,

R_1 is $-(C(R^a)_2)_x-$ or $-O-Si(R^a)_2(C(R^a)_2)_x-$, where each x is independently an integer of 1 to 6 and each R^a is independently a H or C_1-C_6 alkyl, wherein when R_1 is $-O-Si(R^a)_2(C(R^a)_2)_x-$, the O atom of R_1 bonds to Si on A,

X is S, SO, or SO_2,

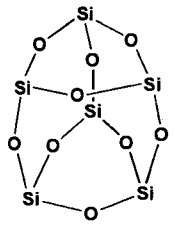
each R_2, R_3, R_4 and R_5, when present, is independently a linear or branched alkyl group of formula C_nH_{2n+1}, where n is from 1 to 30, or a group of formula $Ar(CH_2)_m-$, where Ar is a C_{6-10} aryl or a 5 to 10 membered heterocyclic group containing one or more heteroatoms, where each independently is N, O or S, and m is from 1 to 30; and

each p, q, r and s is independently from 0 to the total number of Si atoms in A, and the sum of p, q, r and s is from 4 to the total number of Si atoms in A.

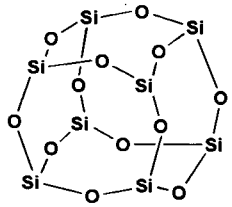
2. The compound of formula (I) according to claim 1, wherein A is a polyhedral oligomeric silsesquioxane (POS).

3. The compound of formula (I) according to claim 1 or 2, wherein the sum of p, q, r and s is 6, 8, 10 or 12.

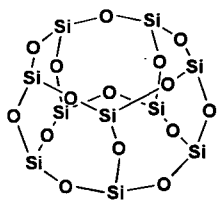
4. The compound of formula (I) according to any one of claims 1 to 3, wherein A is



$(SiO_{1.5})_6$

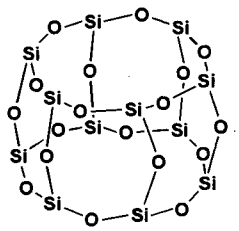


$(SiO_{1.5})_8$



$(SiO_{1.5})_{10}$

or



$(SiO_{1.5})_{12}$

5. The compound of formula (I) according to any one of claims 1 to 4, wherein R_1 is $-CH_2-CH_2-$ and bonds to a Si atom of A.

6. The compound of formula (I) according to any one of claims 1 to 4, wherein R_1 is $-OSi(Me)_2CH_2CH_2-$ and the O atom of $-OSi(Me)_2CH_2CH_2-$ bonds to a Si atom of A.

7. The compound of formula (I) according to any one of claims 1 to 6, wherein each R_2, R_3, R_4 and R_5, when present, is independently a linear or branched alkyl group of formula C_2H_{2n+1}, where n is from 1 to 30.

8. The compound of formula (I) according to any one of claims 1 to 6, wherein each R_2, R_3, R_4 and R_5, when present, is independently a group of formula $Ar(CH_2)_m-$, where Ar is a C_{6-10} aryl group or a 5 to 10 membered heterocyclic group and m is from 1 to 30.

9. The compound of formula (I) according to any one of claims 1 to 8, wherein A is $(SiO_{1.5})_8$.

10. A process for the preparation of a compound of formula (I), as defined in claim 1, 2, 3, 4, 5, 6, 7, 8 or 9, comprising:

- reacting a compound of formula (I') or (I''') with R'-SH, in the presence of a radical initiator,

$$A\text{-}(CH{=}CH_2)_{p+q+r+s} \quad (I') \qquad \text{or}$$
$$A\text{-}(OSi(Me)_2CH{=}CH_2)_{p+q+r+s} \quad (I''')$$

wherein A is as defined in claim 1, 2, 3, 4, 5, 6, 7, 8 or 9, and R' is R_2, R_3, R_4 or R_5, or a mixture thereof.

11. A process for the preparation of a compound of formula (I), as defined in claim 1, 2, 3, 4, 5, 6, 7, 8 or 9, comprising:

- reacting a compound of formula (I'') or (I'''') with R'', in the presence of a radical initiator,

$$A\text{-}(CH_2CH_2\text{-}SH)_{p+q+r+s} \quad (I'') \quad \text{or}$$
$$A\text{-}(OSi(Me)_2CH_2CH_2SH)_{p+q+r+s} \quad (I'''')$$

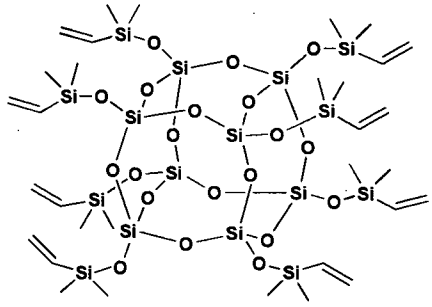
wherein R'' is a precursor of R_2, R_3, R_4 or R_5 and has a terminal unsaturated bond.

12. The process according to claim 10 or 11, wherein the free radical initiator is 2,2-azobis(isobutylcyanate) (AIBN).

13. The process according to claim 10 or 11, wherein the free radical initiator is benzoperoxide (BPO).

14. A lubricant comprising a compound as defined in claim 1, 2, 3, 4, 5, 6, 7, 8 or 9.

15. The compound octa(vinyldimethylsilyl)-POS



Octa(vinyldimethylsilyl)-POS

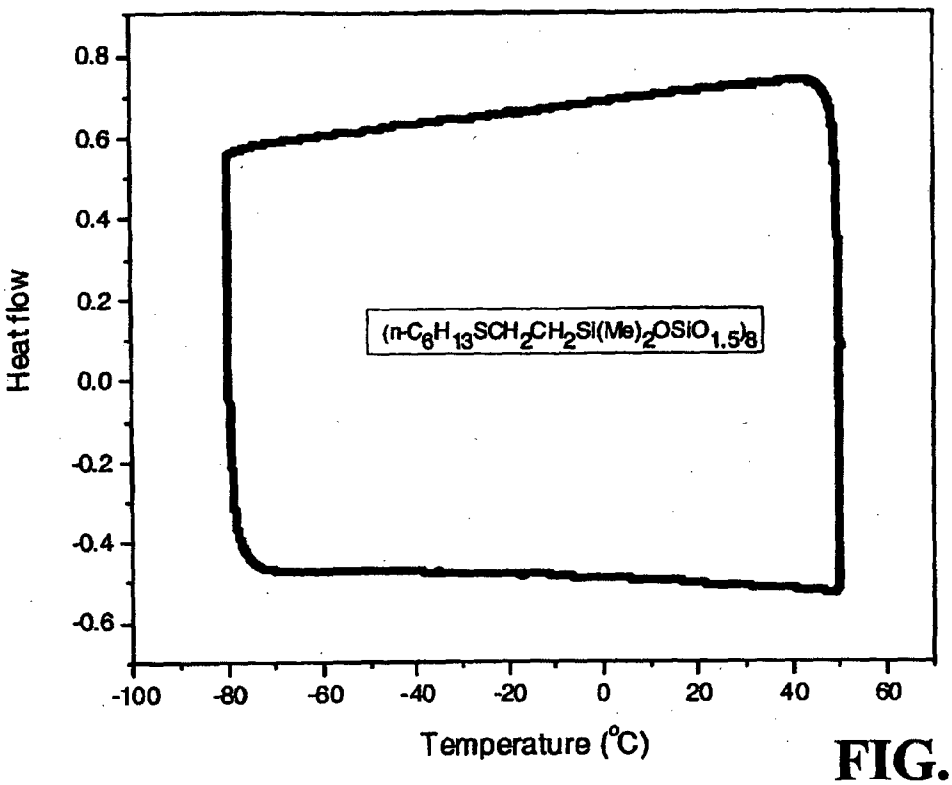

Heat flow
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
(n-C6H13SCH2CH2Si(Me)2OSiO1.5)8
-100
-80
-60
-40
-20
0
20
40
60
Temperature (°C)

FIG. 1

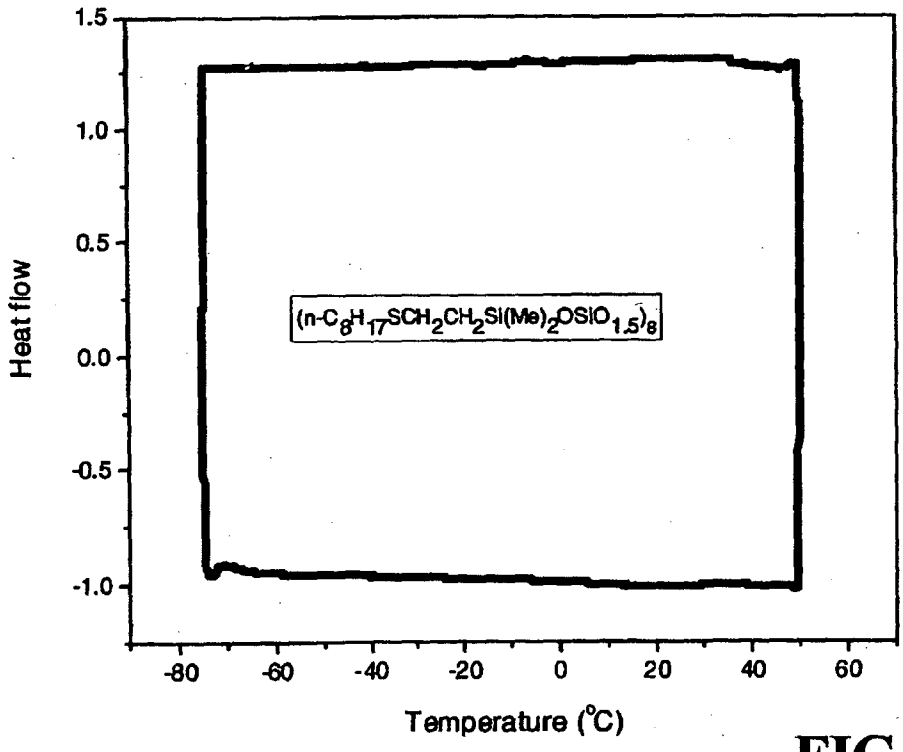

Heat flow
1.5
1.0
0.5
0.0
-0.5
-1.0
(n-C8H17SCH2CH2Si(Me)2OSiO1.5)8
-80
-60
-40
-20
0
20
40
60
Temperature (°C)

FIG. 2

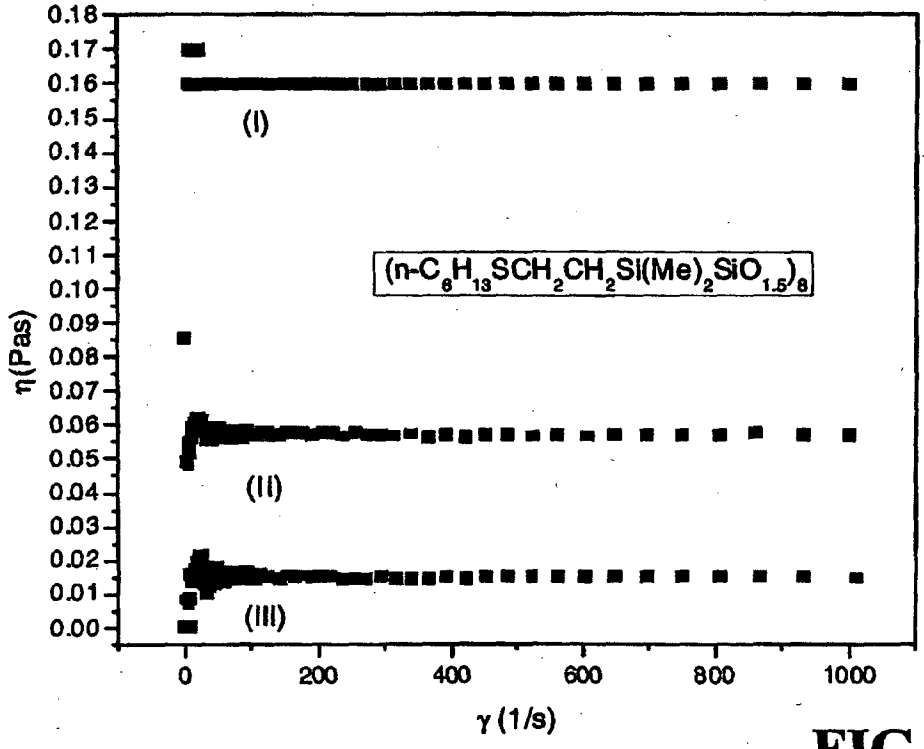

0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
η(Pas)
(I)
(n-C6H13SCH2CH2Si(Me)2SiO1.5)8
(II)
(III)
0
200
400
600
800
1000
γ (1/s)

FIG. 3

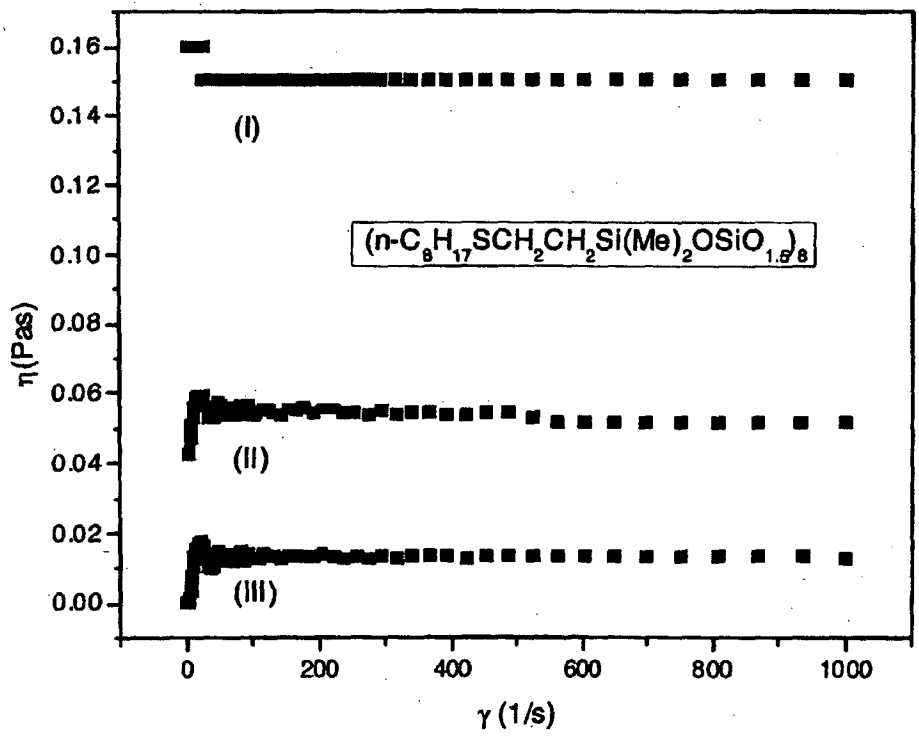

0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
η(Pas)
(I)
(n-C8H17SCH2CH2Si(Me)2OSiO1.5)8
(II)
(III)
0
200
400
600
800
1000
γ (1/s)

FIG. 4

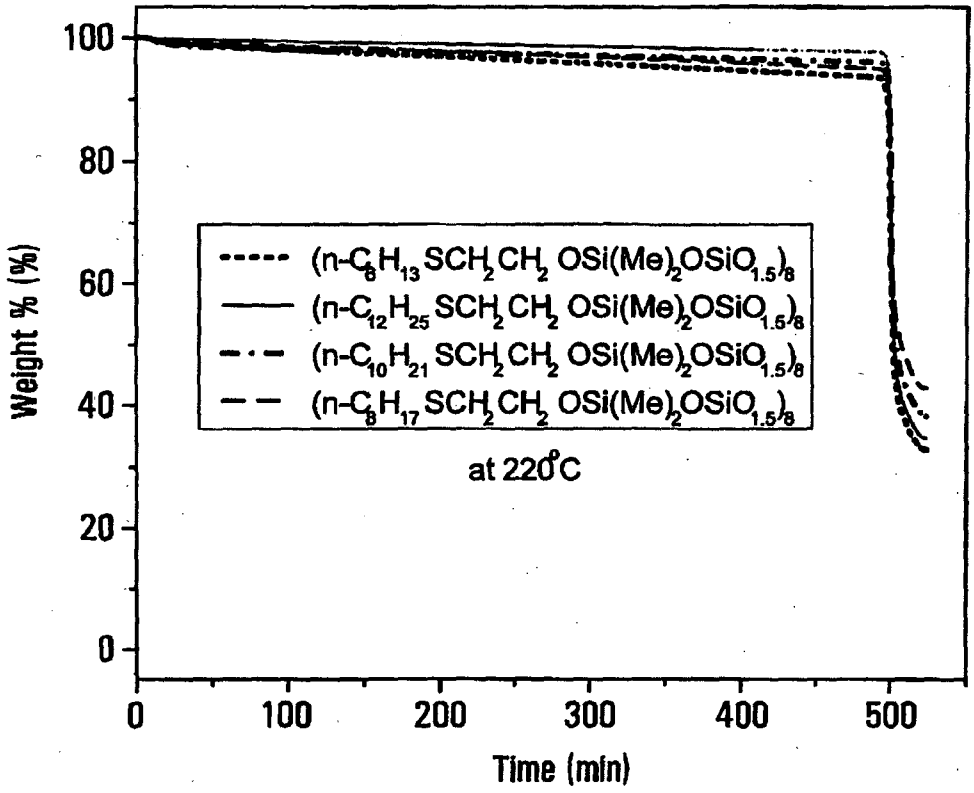

100
80
60
40
20
0
Weight % (%)
0
100
200
300
400
500
Time (min)
(n-C8H13SCH2CH2 OSi(Me)2OSiO1.5)8
(n-C12H25SCH2CH2 OSi(Me)2OSiO1.5)8
(n-C10H21SCH2CH2 OSi(Me)2OSiO1.5)8
(n-C8H17SCH2CH2 OSi(Me)2OSiO1.5)8
at 220°C

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2010/000074

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C07F 7/21 (2006.01) *C10M 139/04* (2006.01)

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)

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)
FILE REGISTRY, CAPLUS: Substructure search based on the core silsesqioxane moiety and containing sulfur, and formula search for Claim 15.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CAPLUS, AN 1995:399450 and U. DITTMAR et al., 'Functionalised octa(propylsilsesquioxanes) (3-XC3H6)8(Si8O12) – model compounds for surface modified silica gel', *Journal of Organometallic Chemistry* (1995), 489 (1-2), 185-94. See Abstract and CAS Registry Number 164017-83-8.	1-4, 7, 9
X	DATABASE CAPLUS, AN 1990:198516 and P. A. AGASKAR, 'Facile, high yield synthesis of functionalised spherosilicates: precursors of novel organolithic macromolecular materials', *Inorganic Chemistry* (1990) 29(9), 1603. See Abstract and CAS Registry Number 126503-69-3.	15

☐ Further documents are listed in the continuation of Box C ☐ See patent family annex

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 March 2010	1 APR 2010
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. +61 2 6283 7999	Authorized officer **L.F. MCCAFFERY** AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : +61 2 6283 2573